Copies of Experimental Evidence and Rule 132 Declarations, Filed In:

U.S. Serial No.: 09/009,455 Inventor: Mills Filed: 01/20/1998

Examiner: Kalafut Art Group: 1745

Today's Date: 30 October 2007

RULE 132 DECLARATION OF DR. RANDELL L. MILLS

I, Randell L. Mills, declare and state as follows:

1. I am the founder and CEO of BlackLight Power, Inc., located at 493 Old Trenton Road, Cranbury, New Jersey 08512.

2. I majored in chemistry and received my bachelor of arts degree, *summa cum laude* and Phi Beta Kappa, from Franklin & Marshall College in 1982. I received a medical degree from Harvard Medical School in 1986. While attending Harvard Medical School, I concurrently spent a year taking courses in advanced electrical engineering at the Massachusetts Institute of Technology. I have also had significant academic training in biology, chemistry, mathematics and physics.

3. I began my research in the field of energy technology over ten years ago. I have authored, co-authored or collaborated on numerous publications, reports and presentations at scientific meetings in the field of energy technology and novel hydrogen chemistry, as shown in the attachment hereto.

4. I am fully qualified to conduct the research that led to the discovery and development of BlackLight's lower-energy hydrogen technology.

5. I personally conducted and/or supervised the experimental data disclosed in the articles submitted to the U.S. Patent and Trademark Office ("PTO"), which are described in the attached list. The coauthors, if any, assisted me in preparing the data.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

By _____
Dr. Randell L. Mills

Date: 3 October 2007

Journal and Book Publications

116. K. Akhtar, J. Scharer, R. L. Mills, "Substantial Doppler Broadening of Atomic Hydrogen Lines in DC and Capactively Coupled RF Plasmas," IEEE Transactions on Plasma Science, submitted.

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9. R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, June 2006 Edition, BlackLight Power, Inc., Cranbury, New Jersey
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Substantial Doppler broadening of atomic-hydrogen lines in DC and capacitively coupled RF plasmas

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The mechanism of extraordinary broadening of the Balmer lines of hydrogen admixed with Ar or He as opposed to Xe in a DC glow discharge and a capacitively coupled rf discharge is studied over a wide range of pressure and gas compositions. High-resolution optical emission spectroscopy is performed parallel to the electrode axis (end-on) and perpendicular to the electrode axis (side-on) along with Langmuir probe measurements of plasma density and electron temperature for the capacitive discharge case. An excessively broad and symmetric (Gaussian) Balmer emission line corresponding to 20-60 eV of hydrogen atom energy is observed in Ar/H_2 and He/H_2 plasmas when compared to the majority species atom temperatures. Energy is transferred selectively to hydrogen atoms whereas the atoms of admixed He and Ar gases remain cold (<0.5 eV). In the field acceleration model that has recently been put forth to explain the broadening [Cvetanovic et. al. J. App. Phys., Vol. 97, 033302-1, 2005], there is neither a preferred ion nor atom and according to this model, one should observe enhanced temperature hydrogen and helium atoms in He/H_2 discharges where the atomic mass is more comparable (4:1). The absence of hot H atoms in Xe/H_2 plasmas also challenges the paradigm of the field acceleration model since Xe is also a noble gas and electronically similar to He. The model of an energetic chemical reaction of hydrogen [Mills et. al *IEEE Trans. Plasma Sci.*, 31, p.338, 2003] as the source of broadening can explain the observation that only the selective heating of hydrogen atoms in certain plasmas exhibits the selective extraordinary broadening and isotropic emission profiles.

I. INTRODUCTION

Substantial Doppler broadening of hydrogen Balmer lines has been observed in pure hydrogen and specific gaseous mixtures of hydrogen with certain heavier atom plasmas produced by DC and capacitively coupled 13.56 MHz radio frequency waves [1-17]. This broadening is caused by the presence of excited hydrogen atoms. In all these instances, energy is transferred selectively to the hydrogen atom whereas the H_2 molecules as well as the He and Ar atoms remain cold. Historically, most mechanisms proposed for excessive H_α broadening in pure hydrogen and mixtures of hydrogen with inert gases [1-14] are explained in terms of energetic ions (H^+, H_2^+ and H_3^+) that are accelerated in the cathode fall region followed by energy transfer to the matrix gas (H and H_2) through charge exchange collisions. However, there are variations in the proposed theoretical explanations of the mechanisms that provide energy to atomic H and cause the observed enhanced blue-shifted H_α spectra width that is symmetric with respect to the red-shifted portion of the emission profile. It should be noted, however, that none of these mechanisms explains the selective transfer of energy to the hydrogen atomic state with the atoms of the admixed gases remaining cold (<0.5 eV).

In a pure hydrogen discharge, the Doppler-broadened profile exhibits the presence of a bimodal (or a tri-modal) distribution of neutral species temperatures [14]. The profile consists of a central peak that corresponds to slow thermal hydrogen atoms with kinetic energies in the range 0.25 to 1.0 eV. The population of warm H atoms (10-20 eV) is evident in the plateau of the Doppler broadened profile along with a population of fast hydrogen atoms (> 40 eV). There is general agreement on the mechanisms proposed for the production of slow H (~0.1-1.0 eV) atoms in the excited n=3 state through the process of dissociative excitation, $H_2 + e^- \rightarrow H_2^* + e^- \rightarrow H^*(n=3) + H$, and dissociative ionization,

$H_2 + e^- \rightarrow 2e^- + H_2^+ \rightarrow H^*(n=3) + H^+$, of hydrogen molecules and electron impact excitation of H atoms, $H + e^- \rightarrow e^- + H^*(n=3)$ [1-2].

There are significant variations in the literature describing the mechanisms proposed to explain the production of hydrogen atoms with energies greater than 20 eV. These were originally proposed to be the result of dissociation of H_2^+ ions in vibrationally excited molecular ground states [2-3]. Recently, the mechanism of charge exchange between ions accelerated in the sheath and neutrals and ion impact on electrodes has been proposed as the source of energetic hydrogen atoms in these discharges. In this model, henceforth called the Collisional Model (CM) [5 and references therein], sheath accelerated H^+ and H_3^+ ions in a hydrogen plasma are proposed to either transfer charge directly to the hydrogen atom or dissociate the H_2 molecule followed by charge exchange collisions to explain the energy spectrum of hydrogen atoms [1-15]. The processes are governed by the following reactions [5-7] where the * indicates excited n=3 atomic state:

$$(H^+)_{fast} + H_{slow} \rightarrow H^*_{fast} + (H^+)_{slow} \qquad (1)$$

$$(H^+)_{fast} + (H_2)_{slow} \rightarrow H^*_{fast} + (H_2^+)_{slow} \qquad (2)$$

$$(H_3^+)_{fast} + H_{slow} \rightarrow H_3 + H^*_{fast} + (H_2^+)_{slow} \qquad (3)$$

$$(H_3^+)_{fast} + (H_2)_{slow} \rightarrow H^*_{fast} + (H_2)_{fast} + (H_2^+)_{slow}. \qquad (4)$$

Since the particle acceleration due to the electric field is directional, the energy gained by a positive ion as it travels towards the cathode will maintain that directionality along with the directed energy of the excited hydrogen atom as long as ion-neutral collision rates are small. This mechanism can only account for the red portion of the spectrum when viewed optically towards the ion accelerating electrode sheath. The observed symmetry in the Gaussian profile of the

hydrogen Balmer line is explained in terms of the sputtered fast H atoms and the back-reflected fast H atoms from the cathode surface [5]. It is argued that this will give rise to a symmetric distribution of energetic H atoms leaving the cathode compared to those accelerating towards the cathode.

In the presence of inert gases, the additional process of charge transfer has been proposed to explain the symmetric H_α broadening [3,12-13]. The introduction of Ar in a pure H_2 plasma increases the Balmer line emission intensity that implies that the concentration of excited hydrogen atoms in the excited n=3 state is also increased. In addition, the fractional population of hot hydrogen atoms obtained from the area under the Gaussian curve implies a concentration in excess of 80 percent of the population in the n=3 state. It has been suggested in the above articles that energetic Ar^+ ions dissociate and ionize H_2 to form ArH^+ that enhances the population of H_3^+ that is proposed as the primary source of atomic hydrogen as shown below when Eq. (6) is combined with Eq. (4).

$$Ar^+ + H_2 \rightarrow ArH^+ + H \qquad (5)$$

$$ArH^+ + H_2 \rightarrow H_3^+ + Ar \qquad (6)$$

The role of metastable argon ions in the enhanced production of H_3^+ ions through the formation of molecular hydrogen ions has also been emphasized [6].

$$Ar^+(3p^5\,^2p^0_{1/2}) + H_2 \rightarrow Ar + H_2^+ \qquad (7)$$

$$H_2^+ + H_2^+ \rightarrow H_3^+ + H \qquad (8)$$

It has been suggested in the above articles that the contribution of these pathways to the significant production of H_3^+ in Ar/H_2 results in an enhanced population of energetic H_{fast} atoms through the processes described in Eqns. (3-4).

However, some of the recent observations [17-26] in DC and capacitively coupled rf discharges are in contrast to the field acceleration based Collisional Models described earlier. For example, it is important to note that, to the best of our search of the scientific literature, no experimental observation has ever been reported, including results in this paper where equally energetic atoms of admixed gases have been found even when the plasma is collisional and mass ratios are comparable. The energy is transferred selectively only to the hydrogen atom whereas the electron energy is less than few eV and admixed gas atoms remain cold (<0.5 eV). It is also very intriguing that no hot H atoms are observed when the admixed gas is xenon. In the CM, the energy of the hot H atom should be independent of the nature of the background gases except for differing collision cross-sections with the background gas. Therefore, it is not possible to readily explain the presence of broadening in argon/hydrogen and helium/hydrogen plasmas along with the absence of broadening in xenon/hydrogen plasmas using this model. In addition, the observation of comparably hot hydrogen atoms in regions outside the plasma sheath requires the local creation of energetic H atoms. As discussed later, the rapid thermalization of H atoms with the background gas due to short ion-neutral collision mean free paths should also confine fast H near the region where it is formed. Therefore, only a process where hot H is produced locally can explain the comparable energies of hot H observed well outside the plasma sheath regions.

It should be noted however, that these observations demonstrate that the source of these hot H atoms is a process fully consistent with the Mills' model of energy production known as Resonance Transfer Model (RTM) [17-26]. The RTM predicts excessive broadening due to a novel energetic chemical reaction of H with certain catalysts involving a two-step energy transfer. First, resonant energy transfer occurs from H to a catalyst and then a second radiative emission or a resonant energy transfer to another H atom that serves as a third body to take away

the remaining reaction energy [19-20]. In this model, it is postulated that the electron in the hydrogen atom that undergoes a 'catalytic' reaction that allows decay from the 'conventional' ground state (principal quantum number, n=1) to a 'fractional' quantum state (e.g. n=1/2). Since the ionization energy of hydrogen is 13.6 eV, two hydrogen atoms can also provide a net enthalpy equal to the potential energy of the hydrogen atom, 27.2 eV— the necessary resonance energy, for a third hydrogen atom to form H (n=1/2).

In order to clarify the underlying mechanism of hydrogen Balmer alpha broadening in hydrogen plasmas and plasmas of hydrogen admixed with noble gases and test the validity of field acceleration based Collisional Model (CM) [5], a comprehensive experiment that covers a wide range of gas pressure and plasma parameters has been performed. A DC glow discharge with pin electrodes and a capacitively coupled radio frequency plasma over a wide pressure range (three orders of magnitude – 10 mTorr to 10 Torr) along with different gas mixture ratios are used to test the ability of the CM to explain the unusual nature of the observed hydrogen broadening. As suggested by the CM, the degree of symmetry of the plasma emission profile should be a function of the electron-neutral and ion-neutral collision frequency and, therefore, should depend on the neutral gas pressure. The CM mandates that observations parallel and perpendicular to the electric field lines yield different emission profiles if the collisional scattering rate is sufficiently small. The experimental setup allows observations both parallel and perpendicular to the electrode axes to test this property. In addition, the presence of hot H atoms was examined in regions far away from the high electric field plasma sheath region near the electrodes. The CM also implies that the energy of hot H atoms is independent of the nature of admixed gases. In contrast, the RTM proposes that the nature of admixed gases will be critical to the broadening mechanism that results in the observed hydrogen emission profile. This aspect is

tested by mixing different gases with hydrogen and observing broadening in the plasma emission profile. In addition to plasma emission spectroscopy, a Langmuir probe is also used to diagnose the capacitive discharge plasma. It should be noted here that the experiments were designed and parameter regimes were considered primarily to test the field acceleration based Collisional Model (CM). In this process, however, the Resonance Transfer Model (RTM) is also tested in light of these new observations.

II. EXPERIMENTAL SYSTEM

The experimental arrangement of the DC discharge is shown in Figure 1. In this configuration, the discharge is created between fine tips of 2% thoriated tungsten electrodes of diameter 1/8 inch spaced 2 cm apart inside either a ½ inch or 1 inch diameter quartz tube. Very fine electrode tips (Fig.1) that are tapered over the last ½ inch to a point are used to minimize the surface area perpendicular to the face of the electrodes. The high E-field near the sharp electrode tip will reduce rapidly as one moves away from it. High-resolution plasma emission spectroscopy is performed through an annulus parallel to the electrode axis along the electric field lines (end-on) and perpendicular to the field lines (side-on). For the end-on observation, plasma emission can be sampled looking towards the anode or cathode. For the side-on observation, an axial scan of the plasma emission is observed in a region adjacent to the cathode rod. Here the cathode tip is located at z=0 cm. The DC plasma setup is placed on an X-Y motion table so that an accurate axial measurement can be carried out without changing the position of the fiber optic bundle. The discharge pressure is maintained in the range of 10 mTorr to 10 Torr. A stabilized negative DC power supply (Kaiser System Inc., Beverly, MA) with voltage and current in the range 0-2000 V and 0-500 mA, respectively, is used to create the plasma. A high

wattage ballast resistor of 20 kΩ is used in series with the power supply to limit the discharge current. Once the discharge is created, the glow discharge is maintained with cathode-anode voltages of 300-400 volts and results in discharge currents in the range of 10-100 mA depending upon the gas pressure, gas flow and discharge configuration.

The capacitively driven radio frequency plasma system consists of a large cylindrical (14 cm ID × 36 cm length) quartz plasma chamber with two electrodes (stainless steel plates of diameter 8.25 cm) placed 1 cm apart at the center (Figure 2). Radio frequency power (13.56 MHz, RF Power Products Inc. NJ, Model RF 5, 500 Watts) is coupled to the electrode using a commercially available impedance matching network (RF VII Inc., Glassboro, NJ). Radio frequency power from the source is fed through the impedance matchbox to the capacitive electrodes using a 1/2-inch diameter steel tube that also facilitates the end-on (parallel to the electric field) observation of plasma through holes in the center of the electrodes. One of the electrodes is permanently grounded. A common ground is maintained for the grounded electrode, rf shield and vacuum system. Two ports in the center of the plasma chamber (Position 2) permit side-on observations of plasma emission 90° and 45° to the electric field. Another side port at the same position allows insertion of a Langmuir probe for plasma density and electron temperature measurements. Plasma emission far away (15 cm) from the high-field plasma sheath region is sampled at Positions 1 and 2. In order to ensure that the plasma emission sampled at positions 1 and 2 have no contribution from the reflected light, the inside of the rf shield enclosure is made non-reflecting.

A helium leak detector (QualyTest, Model: HLT 260, Pfeiffer Vacuum) is utilized to leak test the evacuated plasma chamber. The plasma chamber is maintained with a leak rate below 10^{-7} Torr-L/s. Independent mass flow controllers (MKS) were used to introduce UHP grade

(99.999%) H_2, Ar, He and Xe gases into the plasma chamber through Ultratorr fittings at one end. The chamber pressure for all gas compositions is maintained between 10 mTorr and 10 Torr. An MKS Baratron gauge is used to read the chamber pressure.

III. DIAGNOSTICS

A. Plasma Emission Spectroscopy

Plasma emission from the glow discharge passes through a high-quality UV (200-800 nm) fiber-optic bundle into a monochromator through a 220F matching fiber adapter that is detected either by a photomultiplier tube (PMT) with a stand-alone power supply of 995 volts or by a high quality scientific grade liquid nitrogen cooled CCD arrays. The numerical aperture of the fiber optic bundle is 0.12 and the corresponding acceptance angle is 12^0. The spectrometer utilizes a 1250 mm focal length spectrometer (Jobin Yvon Horiba: Model 1250M Research Spectrometer) with a 2400 g/mm grating and a high resolution of ± 0.006 nm. The spectrometer is rated for an accuracy of ±0.05 nm and repeatability of ±0.005 nm. The spectrometer was scanned through emission profiles of Balmer lines with a step size of 0.01 nm. The entrance and exit slits were set at 20 μm. The liquid nitrogen cooled Symphony model CCD detectors are a family of array detectors from Jobin Yvon with 16 bit ADC with 20 KHz and 1 MHz read out. A back illuminated 2048×512 CCD of 13.5 μm × 13.5 μm size provides very high-resolution capability.

The Doppler-broadened line shapes for atomic hydrogen have been used to calculate the energy of the atomic hydrogen. The motion of a radiating particle moving towards or away from an observer results in a wavelength shift of the emitted line. This broadening is related to the random thermal motion of the emitting atoms and for a Maxwellian velocity distribution it

depends only on the translational (kinetic) temperature. Full half-width, $\Delta\lambda_G$, of the Gaussian profile results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths are $\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2}$. The instrumental half-width $\Delta\lambda_I$ is 0.006 nm and is negligible. The temperature of atomic hydrogen in terms of Doppler ($\Delta\lambda_D$) half-width is given as [27]

$$\Delta\lambda_D = 7.16\times10^{-7}\lambda_0\left(\frac{T}{\mu}\right)^{1/2} \text{ nm.}$$

Here λ_0 is the line wavelength in nm, T is the temperature in K, and μ is atomic mass number(=1 for hydrogen). It can be seen that Doppler broadening is more pronounced for lighter elements at high temperatures. For high densities $>10^{13}$/cc, Doppler broadening competes with Stark broadening. In addition, a contribution to the broadened profile may arise from the mass motion of the plasma. However, for these glow discharges where the plasma density is low ($<10^{11}$/cc), the contribution of Stark broadening to the line shape profile can be neglected without loss of accuracy. We checked the contribution from the mass motion of the plasma by sampling the plasma emission side-on as well as end-on. The absence of line shift shows that the line broadening is primarily due to the thermal motion. In each case, the error in the average Doppler half-width over 10 scans was about ±5% that is attributed to the fluctuations in the plasma. The half-width of the Doppler broadened emission profile was obtained using a multi-Gaussian curve fit utilizing the curve fitting software GRAMS from Jobin Yvon Horiba.

B. Plasma Density Measurement

In the present work, Langmuir probe (LP) data has been used for obtaining the bulk plasma density and bulk electron temperature in the capacitive discharge [28-29]. The cylindrical Langmuir probe is a tungsten tip of radius 1 mm and length 5 mm enclosed in an alumina tube.

The LP is placed between the electrodes at position 2 where most of the plasma heating occurs. In order to characterize the capacitively coupled radio frequency plasma, an rf compensated LP is utilized that allows accurate measurement of bulk electron temperature. The probe filtering does not allow time varying, non-Maxwellian properties of the electron energy distribution to be readily observed. Thus, the possible presence of a small population of hot electrons ($E_e > 20$ eV) in such low-density capacitive discharges at gas pressures above 10 mTorr is not considered in this paper. Data acquisition software written in Lab View is used for automatic transfer from the oscilloscope to the computer. The entire LP data analysis in the present work was undertaken using an interactive graphics based software package developed in MatLab.

IV. EXPERIMENTAL RESULTS

A. DC Discharge

The axial profile of the Balmer H_α line (near 656.3 nm) observed perpendicular (side-on) and parallel to the electrode axis (end-on) looking towards anode as well as cathode is obtained for 1 Torr of Ar/H_2 (95/5%), He/H_2 (95/5%), and Xe/H_2 (95/5%) 300-400 V DC plasmas produced between fine tipped electrodes spaced 2 cm apart. The DC discharge is produced over a wide pressure range (and ion mean free path) of 10 mTorr-10 Torr. Significant broadening was observed for Ar/H_2 and He/H_2 plasmas whereas no broadening was observed for Xe/H_2 plasmas.

Axial profiles of the H_α line for side-on as well as for end-on observations for 1 Torr argon mixed with 5% hydrogen plasma are shown in Fig. 3 and Fig. 4, respectively. The emission profile is isotropic and symmetric. The axial scan is performed parallel to the cathode pin axis with the tip located at z=0. The fiber optic cable entrance aperture is placed perpendicular to the surface of the quartz tube. The sampled plasma volume with an acceptance

angle of 12^0 for 1 inch and ½ inch diameter tubes is 30 mm^3 and 4 mm^3, respectively. The H_α line profiles clearly exhibit a two-component Doppler-broadened profile corresponding to two populations of hydrogen atoms. The central narrow part corresponds to slow hydrogen atoms with temperatures in the range of 0.4-0.5 eV. The broad component of the profile corresponds to fast hydrogen atoms with an average temperature of ~ 40 eV. The fractional concentration of the slow part as obtained by curve fitting is 20-25% and the fast hydrogen component corresponds to 80-75 % indicating that the production of fast hydrogen atoms is substantial. Similar emission profiles are obtained for He/H_2 plasmas where the fast hydrogen atoms have temperatures in the range of 30-40 eV. In contrast, only the slow component (~0.5 eV) of the hydrogen population is observed for Xe/H_2 plasmas (Fig. 5). The axial temperature and population profiles of both fast and slow hydrogen atoms corresponding to the emission profiles in Fig.3 are shown in Fig. 6. It can also be seen from Figs. 3 and 6 that the average width of the two Gaussians of the Doppler broadened profile and hence the average temperature does not change appreciably along the axis. Even though the potential drops primarily near the cathode tip, the population of fast hydrogen atoms (area under the curve) peaks at a distance 2 cm away from the cathode tip. Moreover, the population of fast hydrogen atoms as a fraction of the total population is a minimum (82%) at the cathode tip (z=0) and it increases to 94% at z = 2 cm and remains nearly uniform up to z = 8 cm (Fig. 6). It is noted that the intensity and corresponding plasma density decreases away from the cathode tip (Fig. 3) although the hot hydrogen component increases.

Figure 7 shows the normalized emission profile for an end-on observation in Ar/H_2 and He/H_2 plasmas looking towards the anode. A similar symmetrical emission profile is also obtained when the emission is sampled looking towards the cathode. Reflection of field-accelerated ions in equal measure to the accelerated direction is required by the CM to explain

the absence of either a predominant red or blue wing in the emission profile for the end-on observation. Furthermore, the symmetrical profile cannot be explained by the gas matrix collision effect as no change in the normalized profile symmetry is observed as the gas pressure is varied from 10 mTorr to 10 Torr resulting in a variation of electron-neutral collision frequency by three orders of magnitude (Fig. 8).

The average thermal energy of hot hydrogen atoms as catalytic (Ar, He) and non-catalytic (Xe) gases are added to a 100 mTorr hydrogen plasma DC discharge is shown in Fig. 9. As the fractional concentration of the catalyst gas is increased, the thermal energy of hot hydrogen atoms increases. In contrast, the hot H atom thermal energy decreases sharply with increasing Xe concentration. The absence of H_α broadening with a non-catalyst such as Xe cannot be explained on the basis of the collisional model since the acceleration mechanism should be independent of the ion mass.

In addition, the transfer of energy from the electric field in these admixed plasmas is selectively to hydrogen atoms. Since the mass ratio of He to atomic hydrogen is 4:1, especially for highly collisional plasmas at higher gas pressures, it is expected from the Collisional Model [5] that a correspondingly energetic concentration of helium atoms (Doppler broadened profile) will be present. The Doppler half-width of the 667.82 nm He I line as shown in Fig. 10 is 0.012 nm and it can be accurately resolved by the high-resolution spectrometer with an instrumental half-width of only 0.006 nm. The He atoms' average thermal energy corresponding to a 0.012 nm Doppler half-width is 0.2 eV. No change in Doppler broadening of the 667.82 nm He I line was observed for all pressure and composition ranges studied in these experiments. The absence of hot helium atoms in He/H_2 plasmas where the hydrogen atoms have 30-40 eV energies also contradicts the Collisional Model because the atomic mass ratios are comparable (4:1).

B. Capacitively Coupled RF Discharge

The capacitively coupled radio frequency discharge is characterized using Langmuir probe (LP) and plasma emission spectroscopy diagnostics. The LP is employed to measure electron bulk plasma density (n_e) and electron temperature (T_e) and to determine if a bulk population of high temperature (>5 eV) electrons, not detectable by spectroscopic techniques, exists in our capacitively coupled RF plasmas. A side port at position 2 (Fig. 2) allows the insertion of the LP between the rf electrodes. The on-axis LP measurements are summarized in Table 1 for different noble gases admixed with 10% hydrogen at constant pressure of 100 mTorr. The coupled radio frequency power is maintained constant at 100 W for all the cases. In general, a low-density plasma (~10^{10} cm^{-3}) with bulk electron temperatures of 2-3 eV is observed for all plasma conditions. There is a slight drop (~15-20%) in n_e as well as in T_e as hydrogen is added to the pure noble gas plasmas. It should be noted, however, that we did not observe any high-energy (>5 eV) electron population obtained from the LP measurements. A single temperature bulk electron population characterizes these plasmas. The absence of higher-energy electrons in the higher-field regions between the electrode plates implies that there also are no fast electrons in low field regions far away from the electrodes.

Plasma emission from capacitively coupled rf discharges varied over a wide pressure range is sampled perpendicular to the electric field between the large disc electrodes (Position 2 in Fig. 2) and along the electric field through the 1 cm holes in the electrode plates (end-on). In addition, observations are also made at locations far way from the electrode plates (Positions 1 and 3 in Fig. 2). Isotropic and symmetric H_α line profiles are observed for all three locations, independent of the observation angle relative to the electric field direction. The line profile also

remains symmetric as the gas pressure is varied over a wide range from 10 mTorr to 10 Torr. Line broadening is observed only for Ar/H_2 and He/H_2 plasmas and there is no broadening in comparable control mixtures of Xe/H_2. The energy of the hot H atoms increases with increasing concentration of Ar and He gases whereas it decreases with Xe concentration. For the Ar/H_2 and He/H_2 plasmas the energy is selectively transferred to hydrogen atoms. In addition, the temperature of fast H atoms is quite uniform throughout the plasma chamber.

The average thermal energy of hot hydrogen atoms as a function of Ar, He and Xe concentrations [H_2(x sccm); Ar, He, Xe (y=1-x sccm)] is shown in Fig. 11. A pure hydrogen plasma at 150 mTorr with a 20 sccm flow rate is produced at a coupled rf power level of 200 W. The corresponding thermal energy of the fast hydrogen atoms in this hydrogen plasma is ~ 13-15 eV. Noble gases are introduced into the plasma chamber and the total chamber pressure and flow rate are maintained at 150 mTorr and 20 sccm, respectively, by adjusting the hydrogen and noble gas flow rates. As shown in Fig. 11, the average thermal energy of the hydrogen atom, obtained from symmetric emission profiles, increases from ~13-15 eV to 25-30 eV as the Ar and He fraction is increased. In contrast, the average energy of the hydrogen atom decreases with increasing concentration of Xe.

Figures 12 and 13 show the energy and fractional population of fast hydrogen atoms in Ar/H_2 (95/5%) plasmas as the chamber pressure is varied from 10 mTorr to 10 Torr. Plasma emission is sampled perpendicular to the field between the electrodes and along the field lines through holes in the powered and grounded electrodes. As shown in the figures, the fast hydrogen energy (20-25 eV) and their fractional population (70-80%) in n=3 states remains nearly constant as the gas pressure is varied over three orders of magnitude. Very similar profiles

of fast hydrogen energy (Fig. 14) and fractional population (Fig.15) as a function of pressure are obtained for (95/5%) He/H_2 plasmas.

The presence of hot hydrogen far away from the high field sheath region is in contradiction with the Collisional Model. The plasma emission is sampled at Position 1 and Position 3 (Fig. 2) and angular variation is obtained by rotating the optical probe. The reference is normal to the chamber axis and as the observation angle is varied, plasma emission far away (~ 6 cm) from the electrode region is sampled. As shown in Fig. 16, there is a very small influence of the tilt angle on the hot hydrogen energy for both Ar/H_2 and He/H_2 plasmas. It should be noted here that the symmetry of the emission profile is independent of the angle of observation.

V DISCUSSION

The observations and implications resulting from this study contradict the Collisional Model [5] where excessive H_α broadening in pure hydrogen and mixtures of hydrogen with noble gases is explained primarily in terms of energetic ions (H^+, H_2^+ and H_3^+) accelerated in the cathode fall region followed by energy transfer to the matrix gas (H and H_2) through charge exchange collisions. The character of atomic hydrogen broadening, namely the fast component temperature and the fractional population of the fast hydrogen atoms is quite different for different gas mixtures. In all variations of the collisional model [5], one consistent aspect is that the energy required for selective heating of the hydrogen atoms in plasmas consisting of hydrogen and hydrogen admixed with other gases is locally absorbed by ions from the electric field in the cathode fall region. In the CM at low pressures and collisionality, the emission profile should be dependent on the observation angle relative to the electric field direction. In order to explain the observed symmetry in the emission profile, they have argued that sputtered fast H

atoms and the back-reflected fast H atoms from the cathode surface give rise to fast H concentrations leaving the cathode in the same abundance as that moving towards the cathode.

We summarize the significant results of our experimental observations that are inconsistent with the field acceleration based Collisional Model [5]: 1) Hot hydrogen atoms are observed only for pure hydrogen and specific mixtures such as Ar/H_2 and He/H_2 plasmas whereas no hot H atoms are found when hydrogen is admixed with electronically similar Xe [36]. 2) In the Ar/H_2 and He/H_2 cases, energy is transferred selectively to hydrogen atoms where molecular hydrogen and the admixed gas atoms remain colder (<0.5 eV). 3) The population of neutral H atoms is much hotter (15-40 eV) than any of the charged species ($T_e \sim$ 2-3 eV in capacitive discharge). 4) The emission profile is symmetric over a wide pressure and mean free path range (three orders of magnitude) and is independent of the observation angle relative to the electric field direction. 5) Comparably hot hydrogen atoms are observed in field-free regions far away (up to 15 cm) from the high-field sheath region. In the following sections we discuss the inconsistency of the field acceleration based Collisional Model to account for these results and demonstrate that the Resonance Transfer Model is consistent with these observations.

Let us consider the presence of hot hydrogen atoms that occur only for pure hydrogen and hydrogen admixed with Ar and He plasmas and the absence of hot hydrogen atoms in electronically similar Xe/H_2 plasmas for the entire pressure range from 10 mTorr to 10 Torr. In the field acceleration based Collisional Model, the energy of hot hydrogen atoms should be independent of the nature of the electronically similar background gas except for differing collision cross sections of their ions with H. In order to test the collisional effect of background gases, we consider the cross section data for Balmer alpha and beta line emission from H and H^+ impact reactions on hydrogen (H_2) and our other reacting gases [31-36]. It should be noted that

cross-section data for low energy (< 100 eV) H and H^+ impact on all three reacting gases considered in this paper are not available. Therefore, H_α emission cross-sections from the impact of 100 eV H atoms on noble gas targets $H + X(X = Ar, He, Xe) \rightarrow H_\alpha$ are considered. These are 7×10^{-17} cm^2, 2×10^{-18} cm^2, and 5×10^{-18} cm^2 for Ar, He, and Xe, respectively, [31,33,35]. Similarly, the H_α emission cross-sections from 100 eV H^+ impact $H^+ + X(X = Ar, Xe) \rightarrow H_\alpha$, are 2×10^{-19} cm^2 and 1×10^{-17} cm^2 for Ar and Xe, respectively [32,36]. The emission cross-section data for $H^+ + He \rightarrow H_\alpha$ reaction is not available for H^+ energies below 1.25 keV because of the small magnitude of the photon signals [36]. The cross section for $H^+ + He \rightarrow H_\alpha$ collisions at H^+ energies of 1.25 keV is given as $0.6\pm0.3\times10^{-20}$ cm^2 and it will be much smaller for lower H^+ energies [36].

The CM argues that H^+ ions will travel and be accelerated over longer distances and gain more energy before interacting with the target gas if the cross-section of H^+ impact on the target gas is smaller. As a result, increasingly energetic H^+ ions and, therefore via charge exchange, more energetic H atoms should be observed when the target gas is changed from Xe to Ar to He. Hence, following these arguments, we should observe the most energetic H atoms in the presence of He gas at low pressure. In addition, the H_α emission intensity should be similar for both He and Xe since the H impact cross-sections on He and Xe are similar. However, we observe H atoms of comparable energy (30-40 eV in the DC discharge and 20-25 eV in the capacitive discharge) with either He or Ar as the background gas whereas the H atom energies are only 1-2 eV with Xe. The H_α line intensity is also sharply reduced in Xe/H_2 discharges indicating low atomic hydrogen concentrations in non-RT plasmas. It can be concluded,

therefore, that the collisional model fails to explain the absence of fast H in Xe/H_2 discharges in contrast to its presence in Ar/H_2 and He/H_2 discharges.

These observations are consistent with the RTM which mandates that hot hydrogen atoms will be observed in Resonance Transfer (RT) plasmas where an ion is present that can provide a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen. Hence He^+, and Ar^+ can act as 'catalysts' for the process since the electron ionization energies are an integral multiple of 27.2 eV [24]. Furthermore, as predicted by the RTM, Xe species are incapable of acting as catalysts since the ionization energy for Xe is not an integral multiple of 27.2 eV. As a result we do not observe hot hydrogen atoms in Xe/H_2 plasmas. In addition, the atomic hydrogen concentrations in non-RT plasmas are also low as evidenced by the emission line intensity.

We now consider the observation that the energy is transferred selectively primarily to hydrogen atoms (15-40 eV) whereas the atoms of admixed gases remain cold (<0.5 eV). In the Collisional Model there are neither preferred ions nor atoms and, therefore, one should observe correspondingly hot atoms of the admixed gases along with the hot hydrogen atoms. To our knowledge, no measurement has ever been made where equally hot atoms of admixed gases have been found. In collision dominated plasmas at higher gas pressures where an ion is bound to suffer many collisions with the background gas as it moves towards the cathode and where the mass ratios of the constituent gases are comparable, the presence of correspondingly hot atoms of admixed gases is inferred from the Collisional Model. Let us consider a He/H_2 plasma at 10 Torr with the electron-neutral collision frequency of 3×10^{10} s^{-1} [30]. If in gas mixtures where only a trace amount of hydrogen (~1%) is added to the helium plasma, plasma hydrogen and helium ions will undergo many collisions with the background helium gas as they travel towards

cathode. It should be noted that the recombination rate coefficients of helium and hydrogen ions with energy in the range ≈ 20-30 eV is given by the reaction $He^+ + e \rightarrow He$ and $H^+ + e \rightarrow H$. The two-body recombination rates for these two processes are comparable (α_c=10^{-13} cm^3/s) [37-38]. Therefore, the survival probability of both He^+ and H^+ ions as they travel towards the cathode is comparable. It should be noted, however, that with an atomic mass ratio of 4:1 in helium-atomic hydrogen plasmas, we observe hydrogen atoms with average energies of 30-40 eV whereas helium atoms are cold and have energies less than 0.5 eV (Fig. 10). In contrast, this selective transfer of energy to hydrogen atoms even though other comparable mass ratio ions are present is a cornerstone of the RTM prediction.

As shown in Fig. 16, there is a significant presence of comparably hot hydrogen atoms far away from the high-field plasma sheath regions where most of the potential variation occurs. It is well known that outside the sheath region, where the plasma is largely quasi-neutral, the plasma potential variation is very small. Therefore, in a field free region, the field acceleration CM cannot explain the existence of hot hydrogen up to 15 cm from the electrode. In order to explain the presence of hot H atoms in low field regions, the modified CM [5] requires the presence of fast electrons that produce hot atomic hydrogen with an energy comparable in magnitude to that obtained in the high field region where the source of these atoms are accelerated ions in the sheath. The measured electron temperature using the Langmuir probe located between the rf plates, where most of the electron heating takes place, is ≈ 2-3 eV (Table 1). It is reasonable, therefore, to argue that the bulk of the plasma well away from the electrodes region is cold. Moreover, the tail of the electron energy distribution function comprising high-energy electrons is not observed in the LP measurements for up to – 70 V applied voltages and is definitely negligible in the region far away from the electrodes. Hence, these electrons cannot

produce energetic ions that recombine to form H atoms with energies > 15-20 eV. The cross sections for resonant charge exchange transfer ($Ar^+_{fast} + Ar_{slow} \rightarrow Ar_{fast} + Ar^+_{slow}$ and $He^+_{fast} + He_{slow} \rightarrow He_{fast} + He^+_{slow}$) can be utilized to estimate the distance traveled by an ion produced in the cathode fall region without suffering a charge exchange collision that reduces the maximum energy it can obtain. At 20 eV, the resonant charge exchange transfer cross sections (σ_i) for Ar and He ions are comparable at 2.2×10^{-15} cm^2 and 1.5×10^{-15} cm^2, respectively [39]. The mean free path is given as $\lambda_i = \frac{1}{n_g \sigma_i}$ cm, where n_g, the neutral particle density, is a function of gas pressure. At 10 mTorr, the mean-free path for charge transfer, λ_i, is 0.06 cm. Therefore, the ions produced in the cathode fall region will not maintain their energy over a distance of 15 cm without suffering a charge exchange collision in these plasmas [39]. These ions cannot be the source of hot H atoms in a region far away from the electrodes. Moreover, the radiative lifetime of the hydrogen n=3 state is 10^{-8} s [15] and with an assumed average velocity of 10^6-10^7 cm/s corresponding to hydrogen energies of 1-100 eV, it can only travel a distance of 0.01-0.1 mm before emission and reduced energy. This implies that the observed H_α emission is a result of local excitation. The rapid thermalization of H atoms with the background gas will also localize fast H concentrations to the region where it is formed. Therefore, a mechanism that explains the localized production of hot H over the larger plasma chamber is required. Mills' hypothesis of a catalytic reaction of hydrogen is consistent with the observation of hot H atoms far way from the high field region.

In order to explain the symmetric line emission profile, the CM model mandates the presence of a reflector or divertor. In this model a Gaussian distribution is achieved either by the scattering of hydrogen atoms by the electrode surface or by collisional excitation of H_f on H_2

with large angle scattering [6], where H_f represents the hot hydrogen atoms that have previously collided with the electrode. This implies that the sputtered fast H atoms and the back-reflected fast H atoms from the cathode surface are produced in equal measure to produce a symmetric profile. This requires an "ideal isotropic reflector" to reverse the momentum of a positive ion gained from the electric field to give rise to fast H leaving the cathode in the same abundance as that moving towards the cathode. In addition, according to their model, a "divertor" must also exist such that the ratio of fast H at any given energy towards and away from the cathode remains equal and this must be the case in all directions including the direction perpendicular to the electric field. The interaction of an H atom with a metal surface is quasi-elastic for a large range of targets and energies. The particle and energy reflection coefficients for hydrogen atoms to be reflected back in the energy range of 20-30 eV are only 50% [40]. Therefore, the possibility that backscattered H atoms produced with a comparable distribution to those of the incident H atoms with comparable energy distributions so as to yield a symmetric profile is not feasible. In addition, it is well known that the effective cross section for many small-angle ion-neutral collisions to produce an equivalent deflection is larger than that for single large-angle collision [41]. Hence, this argument is not viable as a mechanism to explain the symmetry of the plasma emission profile.

Electron-ion, electron-neutral, and ion-neutral collision frequencies are a complex function of not only the gas pressure but also of the energy of the colliding particles. Therefore, in order to obtain a better insight into the energy transfer through the collision and charge exchange process, an estimate of the collision frequencies at the pressure and energies of interest is discussed. For a flux of incident electrons with velocities v colliding with a background neutral gas, the collision frequency is given approximately as $\nu_{en} = n_g \sigma v = n_g K \sim 3 \times 10^9 \times P(\text{Torr}) s^{-1}$

where n_g is the neutral number density given by Loschmidt's number and σ is the collision cross-section and K is the rate constant [41-42]. At 10 mTorr and 10 Torr, the electron-neutral collision frequencies are 3×10^7 s^{-1} and 3×10^{10} s^{-1}, respectively, a variation of three orders of magnitude. Therefore at 10 mTorr, the electron-neutral collision frequency is comparable to the rf frequency and the electron can travel to the anode in one rf period of 73 ns. The LP measured electron temperature is 2-3 eV and the electron can travel a distance of about 8 cm during one rf period without suffering collisions with the background neutral gas. Therefore, in low-collision-rate plasmas compared to the ion transit time between the electrodes, based on the CM, fast H atoms produced by the charge exchange process will continue to move towards the direction of the accelerated ions and will yield a predominant red or blue wing in the emission spectrum relative to the direction of observation. However, the data presented in this paper are contrary to the prediction of the CM field acceleration mechanism of energy transfer to hydrogen atom. The symmetric line profile is independent of the angle of observation.

VI CONCLUSION

The mechanism of extraordinary broadening of the hydrogen Balmer lines in hydrogen admixed with noble gases has been studied in two different discharge systems over a wide parameter range to examine highly collisional and weakly collsional regimes. Experiments were performed to test the validity of the field acceleration based Collisional Model. The field acceleration based Collisional Models were formulated to explain the energy gained by hydrogen atoms in experiments where only hydrogen plasmas and plasmas of hydrogen admixed with much heavier noble gases (Ar) were considered. As a result, the selective transfer of energy only to the hydrogen atom was not considered while theories were formulated to explain the

extraordinary broadening. However, we have found that energy is transferred only to hydrogen atoms and not to the admixed gases even when the admixed gas is helium with a mass ratio of 4:1. It was also realized that this energy transfer is not the same even when the admixed gases are electronically similar. For example, hot H atoms are absent when He and Ar are replaced with an electronically similar noble gas Xe. The directionality of energy gained according to the field acceleration based CM mechanism was tested by using sharp tipped electrodes in a DC discharge, thus minimizing the electrode surface area perpendicular to the axis. The plasma emission parallel and perpendicular to the electric field lines was sampled over a wide pressure range. The H_α line profiles were observed to be symmetric in all cases. As discussed earlier, this symmetry can not be explained by the field acceleration based CM model, including its variations where it is argued that equally hot H atoms in equal measure are produced by backscattering with the cathode surface.

Moreover, the Collisional Model utilizes the presence of a plasma sheath where most of the ions are accelerated and these then transfer energy to hydrogen atoms through the charge exchange process. It has been shown in this paper that hot hydrogen atoms are observed far away from the cathode fall regions in plasmas. The presence of hot H in a region where the plasma potential variation is low and plasma electrons are cold (T_e<2 eV), is clearly in contrast to the CM. It is concluded that these observations are consistent with the RT-plasma mechanism.

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TABLE 1

Langmuir probe measurement of plasma density and electron temperature in capacitively coupled radio frequency plasmas at 100 mTorr and 100 W coupled rf power.

Gas Composition	Bulk Plasma Density (cm^{-3})	Bulk Electron Temperature (eV)
Ar	$2\text{-}3\times10^{10}$	2.1-2.4
Ar/10%H_2	$5\text{-}8\times10^{9}$	1.8-2.0
He	$6\text{-}9\times10^{9}$	2.5-3.0
He/10%H_2	$3\text{-}5\times10^{9}$	1.9-2.3
Xe	$2\text{-}5\times10^{10}$	1.7-2.0
Xe/10%H_2	$7\text{-}9\times10^{9}$	1.7-1.9

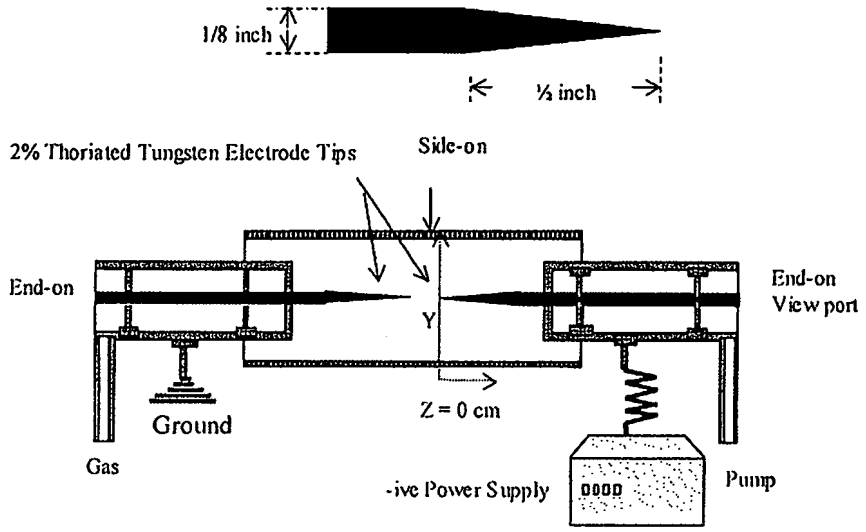


Fig 1. Schematic of the DC discharge created between the fine tips of 2% thoriated tungsten electrodes with the direction of axial scans defined. The cathode tip is taken as z=0 cm for side-on observations measured along the axis of the cathode from its tip to its electrical connection.

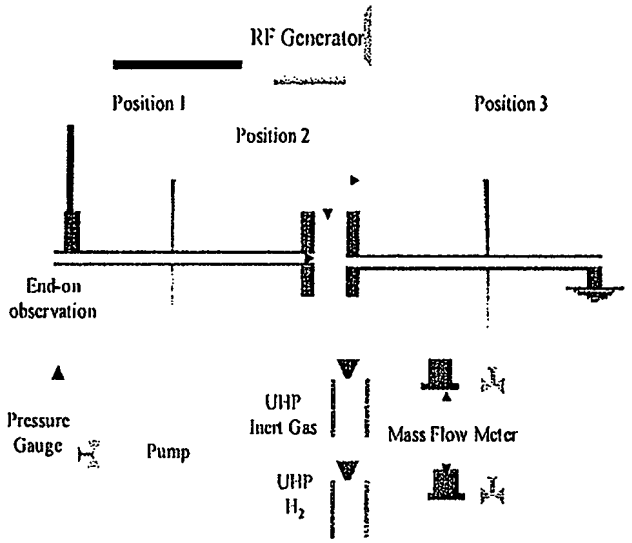


Fig.2: Schematic of the capacitively coupled radio frequency plasma system. Optical emission spectroscopy is performed perpendicular to the electric field (Position 2) and parallel to the field (end-on observation).

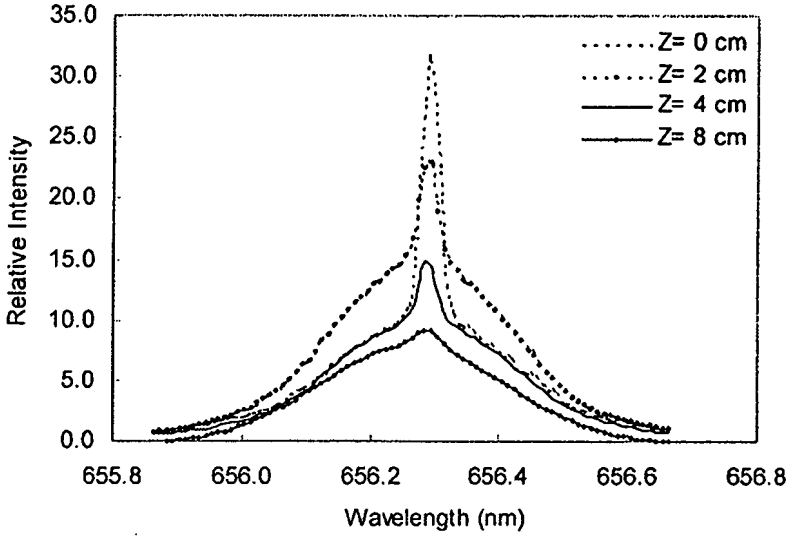


Fig. 3. Axial scan of the 656.3 nm Balmer α line width recorded on a 1 Torr *Ar* /H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA showing 80% of the hydrogen was 'hot' with an average hydrogen atom energy of 40 eV, compared to < 0.5 eV for the slow population.

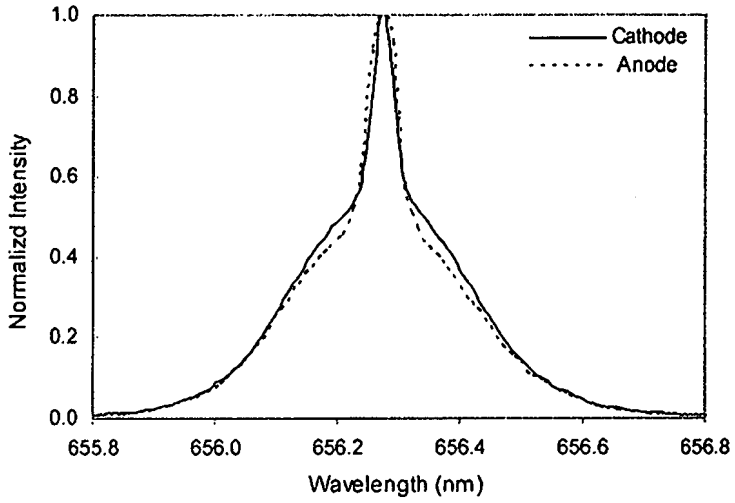


Fig. 4. The 656.3 nm Balmer α line width recorded end-on (parallel to the electric field) on a 1 Torr *Ar* /H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA. Both views looking towards the cathode as well as the anode show a symmetrical emission profile. The temperature of hot hydrogen atoms is in the range of 38-40 eV.

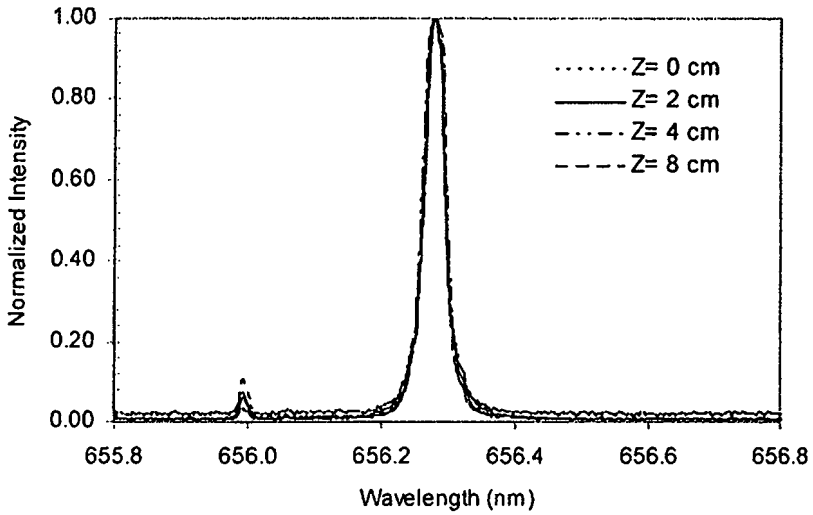


Fig. 5. Axial scan of the 656.3 nm Balmer α line width recorded on a 1 Torr *Xe* /H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA showing only a cold population of <1 eV with a decrease in intensity along the cathode due to a decrease in electron density and energy.

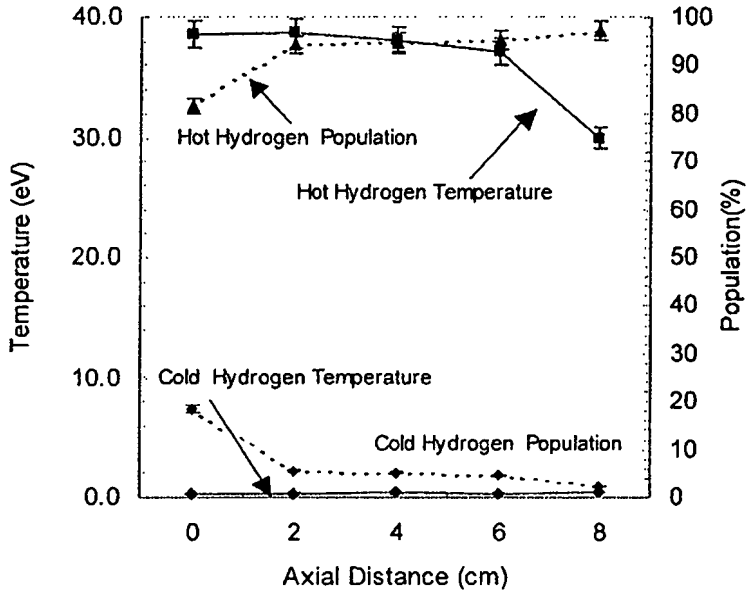


Fig. 6. Axial plots of hot hydrogen atoms temperature and population (given by area under the curve) corresponding to the spectrum in Figure. 3. A hot hydrogen population is present even at a distance of 8 cm away from the cathode tip where most of the potential falls.

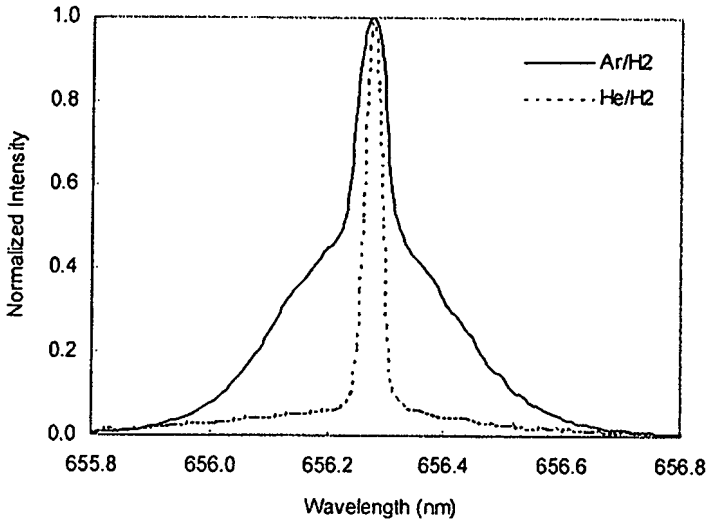


Fig. 7 Normalized end-on emission spectrum of 1 Torr Ar/5%H_2 and He/5%H_2 plasma looking towards the anode. Note the symmetrical emission profile.

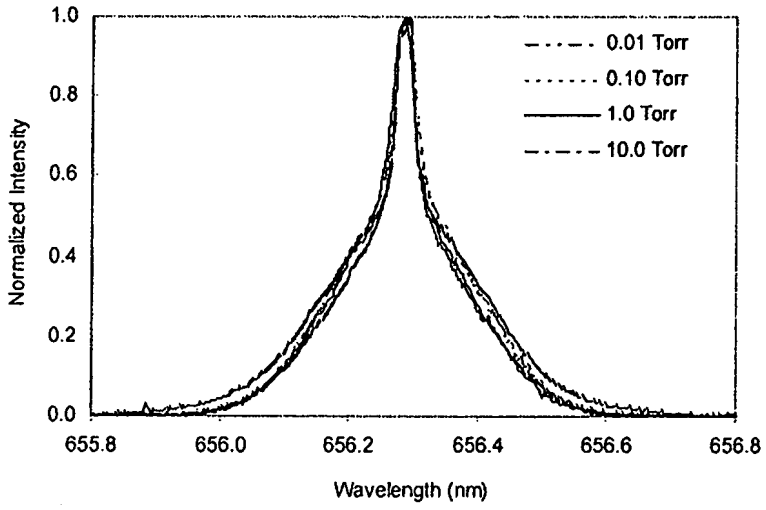


Fig. 8 Normalized end-on emission spectrum of Ar/5%H_2 plasma looking towards cathode as the gas pressure is varied over three-orders-of magnitude from 10 mTorr to 10 Torr. Note the symmetrical emission profile.

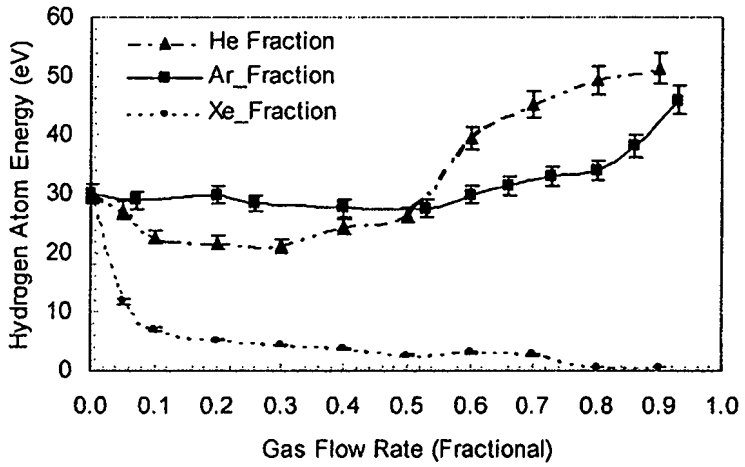


Fig.9 Energy of hot hydrogen atoms as a function of fractional concentration of admixed gases in a DC discharge at 100 mTorr. Note the increase in the energy of hot H as Ar and He concentration increases and decrease in energy with the addition of Xe.

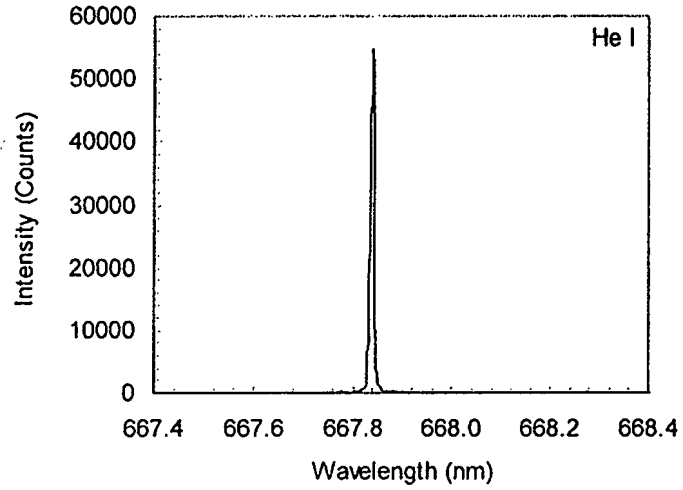


Fig. 10

Fig. 10 The 667.816 *nm* He I line width for 1 Torr He/H_2 (95/5%) at 400 V and 20 mA . No broadening was observed,

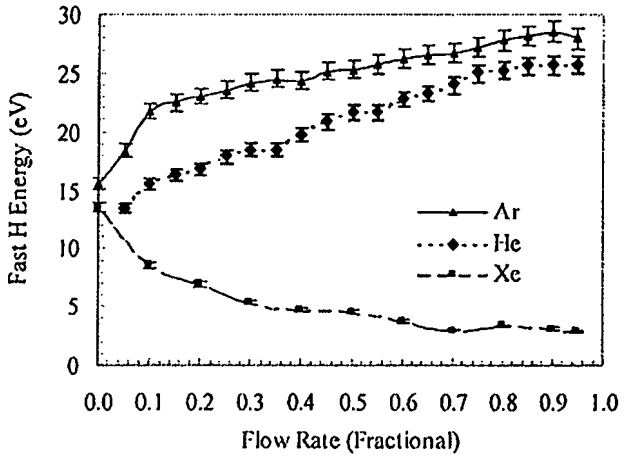


Fig.11. Energy of hot hydrogen atom in Ar/H_2, He/H_2 and Xe/H_2 plasmas as a function of the noble gas concentration [H_2(x) Ar, He, Xe(y=1-x)] in capacitively coupled rf discharge. The plasma chamber is maintained at 150 mTorr with a total flow rate of 20 sccm. The coupled rf power is 200 Watt. H_α emission is sampled perpendicular to the electric field between the capacitive plates.

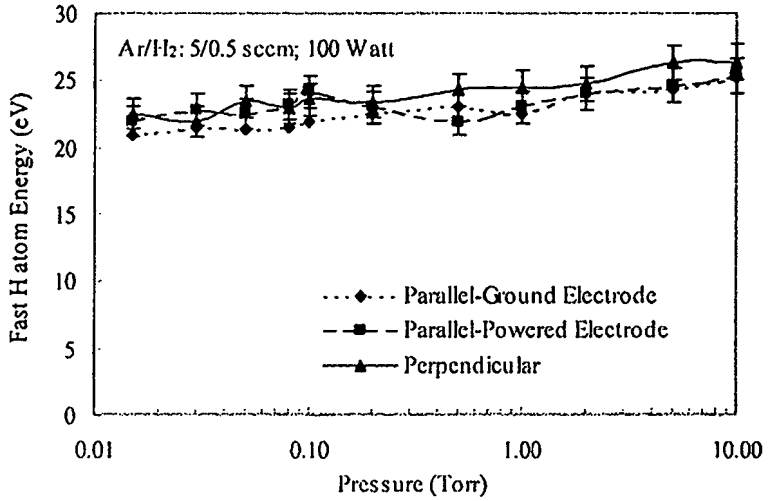


Fig. 12: Hot hydrogen atom temperature for capacitively coupled Ar/H_2 discharge at different gas pressures. Observations are made perpendicular to the field between the electrodes and parallel to the field lines through holes in both powered and grounded electrodes.

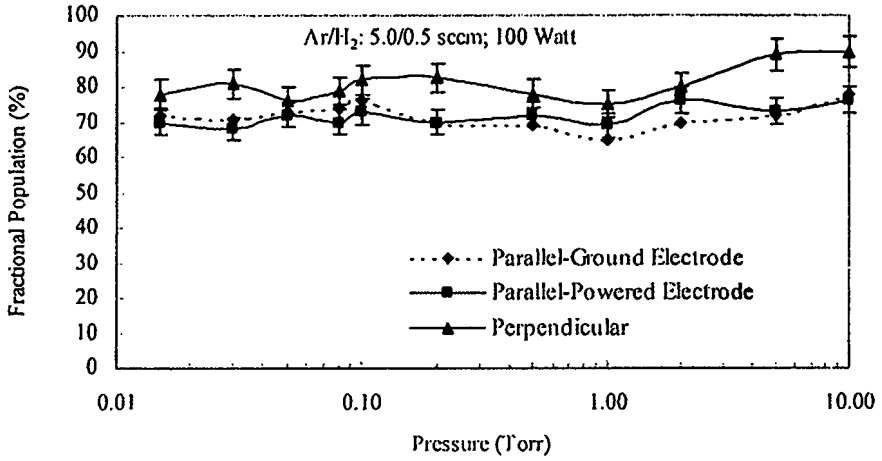


Fig.13. Fractional population of hot hydrogen atoms in n=3 excited state in a capacitively coupled Ar/H_2 discharge at different gas pressures.

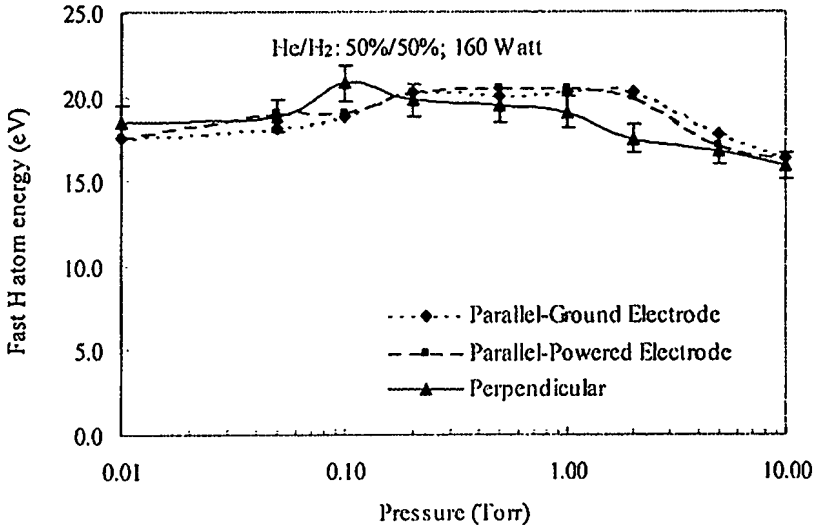


Fig.14. Hot hydrogen atom energy in a capacitively coupled He/H_2 discharge at different gas pressures.

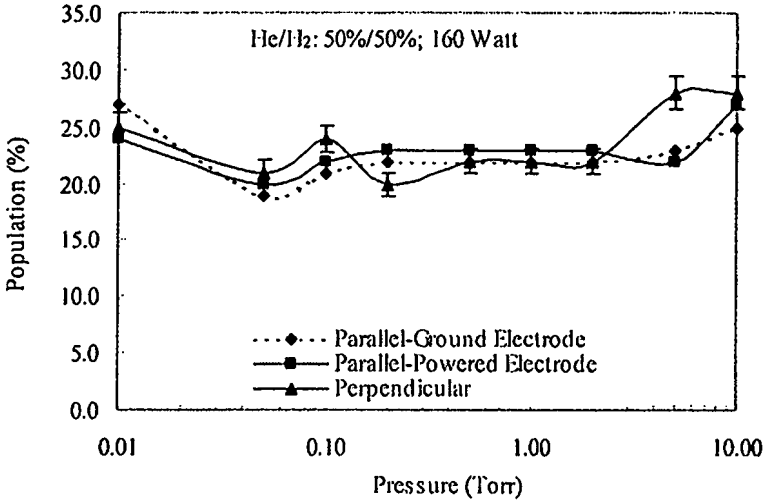
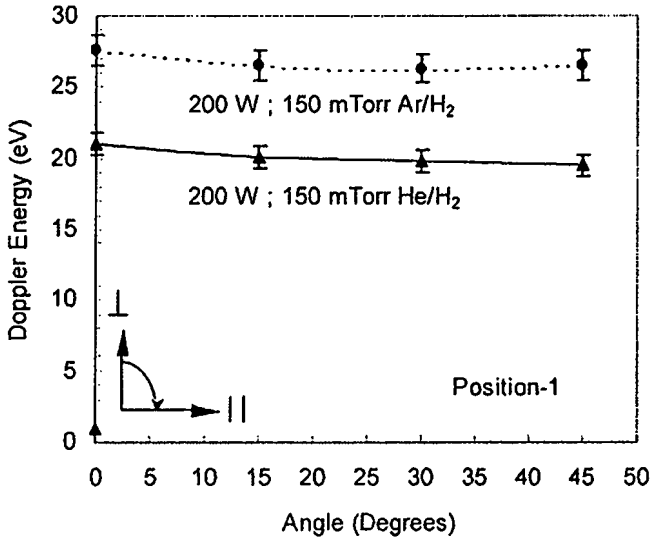
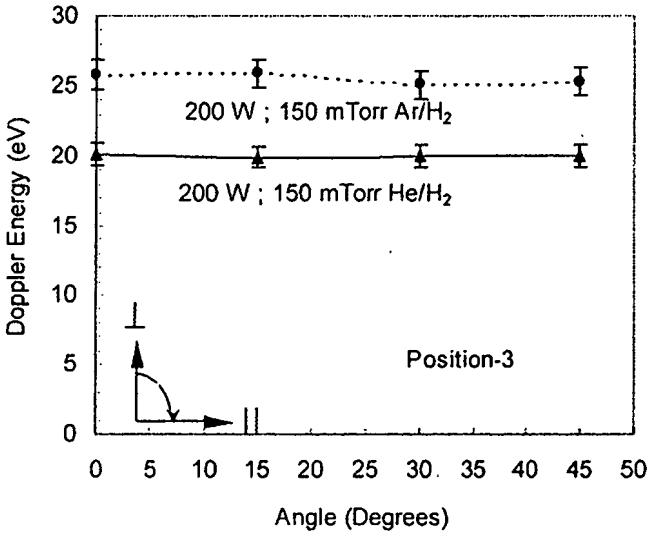


Fig.15. Fractional population of hot hydrogen atoms (n=3 state) in a capacitively coupled He/H_2 discharge at different gas pressures.



(a)



(b)

Fig.16. Angular variation of Doppler energy of hot hydrogen atom in a capacitively coupled radio frequency discharge at 150 mTorr 50%Ar/50%H_2 and 50%He/50%H_2 plasma at 200 W. Plasma emission is sampled at Position 1 (Fig. a) and Position 3 (Fig. b) far away from the region of high field in plasma sheath. Reference is normal to the chamber axis.

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Water Bath Calorimetry on a Catalytic Reaction of Atomic Hydrogen

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ABSTRACT

Plasmas of certain catalysts such as Sr^+ and Ar^+ mixed with hydrogen were studied for evidence of a novel energetic reaction. These hydrogen plasmas called resonant transfer- or rt-plasmas were observed to form at low temperatures (e.g. $\approx 10^3\ K$) and extraordinary low field strengths of about 1-2 V/cm when argon and strontium were present with atomic hydrogen. Time-dependent line broadening of the H Balmer α line was observed corresponding to extraordinarily fast H (25 eV). When an argon-hydrogen hollow-anode glow discharge plasma with strontium metal contained in the cell was optimized for Sr^+ emission, an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population and an excess power of 28.5% of the input power were observed. Using water bath calorimetry, an excess power of 2.85 W was measured on rt-plasmas with Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present. The energy balance was high. Given an argon-hydrogen (95/5 %) flow rate of 1.0 sccm and an average excess power of 2.85 W and energy balances of over $-7.7\ X\ 10^4\ kJ/mole\ H_2$ were measured.

Keywords: catalysis, rt-plasma, fast H, excess power

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1. Introduction

A new chemically generated or assisted plasma source has been developed that is based on a resonant energy transfer mechanism (rt-plasma). One such source operates by incandescently heating a hydrogen dissociator and a catalyst to provide atomic hydrogen and gaseous catalyst, respectively, such that the catalyst reacts with the atomic hydrogen to produce a plasma. It was extraordinary that intense EUV emission was observed by Mills, et al. [1-4] at low temperatures (e.g. $\approx 10^3\ K$) and an extraordinary low field strength of about 1-2 V/cm from atomic hydrogen and certain atomized elements or certain gaseous ions, which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $27.2\ eV$. A number of independent experimental observations [1-26] confirm that the rt-plasma is due to a novel reaction of atomic hydrogen which produces as chemical intermediates, hydrogen atoms in fractional quantum states that are at lower energies than the traditional "ground" ($n=1$) state. Power is released, and the final reaction products are novel hydride compounds. The supporting data include EUV spectroscopy [1-7, 10, 14-20, 23], characteristic emission from catalysts and the hydride ion products [1-4, 14, 16-20], lower-energy hydrogen emission [5-7, 23], chemically formed plasmas [1-4, 14-20], Balmer α line broadening [1-6, 8-14, 16, 19-20, 23], population inversion of H lines [19-21], elevated electron temperature [6, 8-9], anomalous plasma afterglow duration [14-15], power generation [6, 10, 14, 22-23], and analysis of novel chemical compounds [14, 24-26].

The theory given previously [27-29] is based on applying Maxwell's equations to the wave equation. The familiar Rydberg equation (Eq. (1)) arises for the hydrogen excited states for $n>1$ of Eq. (2).

$$E_n = -\frac{e^2}{n^2 8\pi\varepsilon_o a_H} = -\frac{13.598\ eV}{n^2} \tag{1}$$

$$n = 1, 2, 3, \ldots \tag{2}$$

An additional result is that atomic hydrogen may undergo a catalytic reaction with certain atoms and ions, which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2\ eV$, wherein m is an integer. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots, \frac{1}{p};\quad p \text{ is an integer} \tag{3}$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n=1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states, say $n=1$ to $n=1/2$, is possible via a

nonradiative energy transfer. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2\ eV$ (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms and releases the energy to the surroundings to affect electronic transitions to fractional quantum energy levels). As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy as $q \cdot 13.6\ eV$ emission [5-7] or $q \cdot 13.6\ eV$ transfer to H to form extraordinarily hot, excited-state H [8-13] until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (3). Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common [30]. Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling [31].

Certain atoms, excimers, and ions which provide a reaction with a net enthalpy of an integer multiple of the potential energy of atomic hydrogen, $E_h = 27.2\ eV$ where E_h is one hartree. Specific species (e.g. He^+, Ar^+, K, and Sr^+) identifiable on the basis of their known electron energy levels are required to be present in plasmas with atomic hydrogen to catalyze the process. In contrast, species such as atoms or ions of Mg or Xe do not fulfill the catalyst criterion—a chemical or physical process with an enthalpy change equal to an integer multiple of E_h that is sufficiently reactive with atomic hydrogen under reaction conditions.

Ar^+ may serve as a catalyst since its ionization energy is about $27.2\ eV$. Also, since the ionization energy of Sr^+ to Sr^{3+} has a net enthalpy of reaction of $2 \cdot 27.2\ eV$, Sr^+ may serve as catalyst alone or with Ar^+ catalyst. It was reported previously that an rt-plasma formed with a low field (1V/cm), at low temperatures (e.g. $\approx 10^3\ K$), from atomic hydrogen generated at a tungsten filament and strontium which was vaporized by heating the metal [1-4]. Strong VUV emission was observed that increased with the addition of argon, but not when sodium, magnesium, or barium replaced strontium or with hydrogen, argon, or strontium alone. Characteristic emission was observed from a continuum state of Ar^{2+} at $45.6\ nm$ without the typical Rydberg series of Ar I and Ar II lines which confirmed the resonant nonradiative energy transfer of $27.2\ eV$ from atomic hydrogen to Ar^+ [2, 4, 18]. Predicted Sr^{3+} emission lines were also observed from strontium-hydrogen plasmas [2, 4] that supported the rt-plasma mechanism.

Significant Balmer α line broadening corresponding to an average hydrogen atom temperature of 14 eV and 24 eV was observed for strontium and argon-strontium rt-plasmas and 23-45 eV for discharges of strontium-hydrogen, helium-hydrogen, argon-hydrogen, strontium-helium-hydrogen, and strontium-argon-hydrogen, compared to $\approx 3\ eV$ for pure hydrogen, krypton-hydrogen, xenon-hydrogen, and magnesium-hydrogen. To achieve that same optically measured light output power, sodium-hydrogen, magnesium-hydrogen, and barium-hydrogen mixtures required 4000, 7000, and 6500 times the power of the strontium-

hydrogen mixture, respectively, and the addition of argon increased these ratios by a factor of about two. A glow discharge plasma formed for strontium-hydrogen mixtures at an extremely low voltage of about 2 V compared to 250 V for hydrogen alone and sodium-hydrogen mixtures, and 140-150 V for magnesium-hydrogen and barium-hydrogen mixtures [1-2, 4]. These voltages are too low to be explicable by conventional mechanisms involving accelerated ions with a high applied field.

To further characterize argon-strontium rt-plasmas, plasma formation was studied relative to mixtures of hydrogen and a chemically similar control that does not have electron ionization energies which are a multiple of $27.2\ eV$, and the Balmer lines were recorded by visible spectroscopy to confirm that an energetic hydrogen plasma was present having H energy states greater than 12 eV corresponding to $n \geq 3$ in Eqs. (1-2). The broadening of the Balmer α line was also recorded as a function of time, and thermal power balance measurements were performed. The cell comprised a titanium or tungsten filament to heat and vaporize some strontium as a source of catalyst and to dissociate molecular hydrogen to atomic hydrogen. The addition of argon to the plasma further provided the catalyst Ar^+.

Since a conventional discharge power source was not present, the formation of a plasma would require an energetic reaction. The origin of Doppler broadening is the relative thermal motion of the emitter with respect to the observer—in this case the spectrometer. Line broadening is a measure of the atom temperature, and a significant increase was expected and observed for catalysts from strontium or argon with hydrogen. The observation of a high hydrogen temperature with no conventional explanation would indicate that an rt-plasma must have a source of free energy. An energetic chemical reaction was further indicated since it was found that the broadening is time dependent. Therefore, the thermal power balance was measured calorimetrically. To maintain a constant level of ionized argon and strontium as catalysts, a DC glow discharge of plasma of argon-hydrogen (97/3%)-strontium was maintained using a hollow anode. The energy balance was measured by water bath calorimetry. We report the results of these characterizations and discuss the implications regarding the rt-plasma mechanism in Secs. 3A-C.

2. Experimental

Balmer Line Broadening. An argon-hydrogen (97/3%)-strontium rt-plasma was generated in the experimental set up (Figure 1) described previously [1-4] comprising a thermally insulated quartz cell with a cap that incorporated ports for gas inlet, and outlet. A titanium filament (55 cm long, 0.5 mm diameter) that served as a heater and hydrogen dissociator was in the quartz tube. 2.5 g of magnesium or strontium metal (Alfa Aesar 99.95%) was placed in the center of the cell under one atmosphere of dry argon in a glovebox.

The cell was sealed and removed from the glovebox. The cell was maintained at 50 °C for four hours with helium flowing at 30 sccm at a pressure of 0.6 Torr. The filament power was increased to 120 W in 20 increments every 20 minutes. At 120 W, the filament temperature was estimated to be in the range 800 to 1000 °C. The external cell wall temperature was about 700 °C. The cell was then operated with and without an argon-hydrogen (90/10%) flow rate of 5.5 sccm maintained at 0.6 Torr. Additionally, the cell was operated with hydrogen and argon-hydrogen (90/10%) gas flow and no metal. Each metal was vaporized by the filament heater. The presence of a hydrogen plasma was determined by recording the visible spectrum over the Balmer region with a Jobin Yvon Horiba 1250 M spectrometer with a PMT detector described previously [8-9] using entrance/exits slits of 200/100 μm, 0.1 Å step size, and a 3 s integration time. The width of the 656.3 nm Balmer α line emitted from the argon-hydrogen (90/10%)-strontium rt-plasma having a titanium filament was measured initially and periodically during operation. The Balmer profile was also recorded on the air-gap, glow discharge reactor described in the next section with an input power of 20 W (V=200; I=0.1A).

Power balance measurements. The power balance of a rt-plasma of strontium with argon-hydrogen mixture (95/5%) maintained in an air-gap, glow discharge reactor shown in Figure 2 was measured by water bath calorimetry using the experimental setup shown in Figure 3. Excess power was observed from argon-hydrogen-strontium plasmas compared to calibration control experiments with the same input power.

The reaction cell comprised a cylindrical stainless steel case of 5.1 cm OD and 17.2 cm in length welded to a set of high vacuum, 8.6 cm diameter Con-flat flanges, as shown in Figure 2. A silver plated copper gasket was placed between a mating flange and the cell flange. The two flanges were clamped together with 10 circumferential bolts. The top-mating flange had a radial centered stainless steel hollow feed through that extended 8.6 cm into the cell and was partially covered by a 3.6 cm long ceramic sleeve, measured from the flange. Gas was fed into the cell by a 1 cm OD stainless steel tube welded to the top-mating flange. Gas flow was controlled by a 0-20 sccm range mass flow controller (MKS model M100B21CS1BV). The cell pressure was monitored by a 0-10 Torr MKS Baratron (model 626A11TEE) absolute pressure gauge. Additionally, the top-mating flange had a drilled thermo well that housed a stainless steel thermocouple (0.3 cm OD). Two 1 cm OD stainless steel tubes were welded to the bottom wall of the reaction cell. One carried the exhaust gas, and the other served as a connection port for a 0.6 cm OD and 16.5 cm long quartz rod to perform optical emission spectroscopy studies. In an oxygen free environment (glove box), 4 grams of strontium distributed in 15 pieces was loaded into the reaction cell and placed below the hollow electrode

as shown in Figure 2, the reaction cell was transferred into the stainless steel jacket, and all the gas and electrical connections were fitted and checked for leaks.

The reaction cell was housed inside a cylindrical stainless steel jacket of 15.2 cm OD and 30.5 cm in length with a removable front flange having welded Ultratorr connectors that fit the reaction cell gas line and the thermocouple. The bottom wall of the stainless steel jacket had two welded Ultratorr connections that fitted the reaction cell exhaust gas and the quartz rod connection port. Two 0.41 cm OD copper power feed-throughs were welded on the side wall and that provided electrical connectors for the reaction cell when it was placed inside the stainless steel jacket. The jacket housing containing the reaction cell was placed inside the drained water bath container, the gas inlet and outlet tubes were connected to the gas/vacuum manifold, as shown in Figure 3.

The water bath (Figure 3) comprised an insulated reservoir filled with 41 liters of de-ionized water. The water was agitated with a paddle driven by a stirring motor. A high precision linear response thermistor probe (Omega OL-703) recorded the temperature of the water bath as a function of time for the stirrer alone to establish the baseline. The water bath was calibrated by a high precision heater (Watlow LGEX17B Type CR-1, with a Xantrex XDC power supply 0-6000 ± 0.01 W). Each experiment comprised three distinctive periods: pre-period, heating period, and post period. The pre-period was performed with no power applied to the electrode or to the heater during the reaction test or calibration test, respectively. During the heating period, power was applied through the electrode or through the heater. In the post period, the power applied during the heating period was turned off. The water of the bath was agitated with a stirrer spinning at constant speed throughout all three periods.

The heat capacity was determined for several input powers, 10, 20, 30, 40, and 50 W ± 0.01 W, and was found to be independent of input power over this power range within ± 1.8 %. The temperature rise of the reservoir as a function of time gave a slope in °C/s. This slope was baseline corrected for the stirrer power and loss to ambient. The constant known input power (J/s), was divided by this slope to give the heat capacity in J/°C. Then, in general, the total power output from the cell to the reservoir was determined by multiplying the heat capacity by the rate of temperature rise (°C/s) to give J/s.

The power balance for a plasma system consisting of the contents of the water bath calorimeter is [23]

$$\dot{H} = \dot{M}\left(\hat{H}_{in} - \hat{H}_{out}\right) + \dot{Q}_{plasma} + \dot{Q}_{power\ cable} + \dot{Q}_{stirrer} + \dot{Q}_{heat\ exchange} \quad (4)$$

where H's are enthalpy values (inlet and outlet gases as indicated by the subscripts in and out, respectively, and the hat designates per mole), $\dot{M}$ is the molar flow rate, and the $\dot{Q}$'s are heat flow rates. It is clear from Eq. (4) that a correction must be considered both for the gas flow term (first term, right side), '$\dot{Q}_{power\ cable}$' which represents the input of the section (approx. 80 cm long) of the power cable that passes through the water bath as it brings power to the discharge, for the work of the stirrer, and for the heat exchange between the insulated water bath and its surroundings.

The values of '$\dot{Q}_{power\ cable}$' and the heat carried out with the gas were small, as determined by appropriate temperature readings. Thermocouples were employed to measure the temperature of the input and output gas, as well as the temperature of the power cable just outside the water bath. Given that the temperature of the power cable was the same as the water bath, $\dot{Q}_{power\ cable}$ was taken as zero. The gas temperature change between input to the plasma and output from the water bath was never more than 1 K. Heat transfer from cell containing the flowing gas to the water in the bath was clearly very efficient. Given the flow rate was 1 sccm, this requires a maximum correction of less than 10^{-6} W, a trivial correction. The stirrer and heat exchange terms were found to be the most significant correction, but its value was readily determined by measuring the temperature rise with only the stirrer operating. This correction can be accurately calculated from the slope of the pre- and post-heating periods and was found to be constant, 5.0 W for all experiments. Once these relatively trivial corrections are made, the 'effective' energy balance becomes:

$$\dot{H} = \dot{Q}_{plasma} \quad (5)$$

The calibration procedure resulted in a linear change in temperature for constant power inputs. This is expected, given the nearly constant heat capacity of water over small changes in temperature (<14 K in all cases). Thus, changes in enthalpy can be readily equated with change in temperature of the bath. In short:

$$\dot{H} = C_p\dot{T} = \dot{Q}_{plasma} \quad (6)$$

Thus, one must only multiply the calibration constant by the rate of change of bath temperature to obtain the plasma's heating power of the water bath. In the event that the change in temperature is nearly linear with time, as it was in all cases in this study, the rate (W) of heat input from the plasma to the bath can be readily determined, and compared with the input power. The rt-plasma results were compared with the results of the calibration control experiment determined using the same analytical procedure .

Since the cell and water bath system were adiabatic, the general form of the power balance equation with the possibility of excess power is:

$$P_{in} + P_{ex} - P_{out} = 0 \tag{7}$$

where P_{in} is the input discharge or heater power, P_{ex} is the excess power generated from the hydrogen catalysis reaction, and P_{out} is the thermal power loss from the cell to the water bath. The plasma voltage and current reached steady state in about 5 to 10 minutes after the heating period started, and the temperature measured at the wall of the cell typically reached a steady state in about 1 to 2 hrs after the heating period was started. At this point, the power lost from the cell P_{out} was equal to the power supplied to the cell, P_{in}, plus any excess power P_{ex}.

$$P_{in} + P_{ex} = P_{out} \tag{8}$$

Since the cell was surrounded by water that was contained in an insulated reservoir with negligible thermal losses as discussed above, the temperature response of the thermistor T as a function of time t was modeled by a linear curve

$$\dot{T}(t) = a^{-1} P_{out} \tag{9}$$

where a is the heat capacity (J/°C) for the least square curve fit of the response to power input for the control experiments ($P_{ex} = 0$). The slope was recorded for about 25 hours after the cell was started, to achieve an accuracy of ± 1.8%.

The slope of the temperature rise as a function of time was recorded for each run and baseline corrected for the stirrer power and loss to ambient, then the output power was calculated from the corrected slope. After the calorimeter was calibrated, $T(t)$ was recorded with a selected power to the plasma and compared to the results of identical input to the heater in a separate run of the identical system. The higher slope produced with argon-hydrogen-strontium plasma, having Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present was representative of the excess power. In the case of the catalysis run, the total output power P_{out} was determined by solving Eq. (9) using the measured $\dot{T}(t)$ and the heat capacity a. The excess power P_{ex} was determined from Eq. (8).

3. Results and discussion

A. RT-plasma emission

An argon-hydrogen (90/10%)-strontium rt-plasma formed with a low field (1V/cm), at low temperatures (e.g. $\approx 10^3\ K$), from atomic hydrogen generated at a titanium filament and strontium which was vaporized by heating the metal. H Balmer emission corresponding to population of a level with energy $>12\ eV$ was observed as shown in Figure 4 which also requires that Lyman emission was present. No plasmas formed when magnesium replaced strontium or with hydrogen, argon/hydrogen, or strontium alone. This result indicates that the

emission was due to a reaction of hydrogen with vaporized strontium. No possible chemical reactions of the titanium filament, the vaporized strontium, and 0.6 Torr argon-hydrogen mixture at a cell temperature of 700°C could be found, which accounted for the Balmer emission. In fact, no known chemical reaction releases enough energy to excite Balmer and Lyman emission from hydrogen. In addition to known chemical reactions, electron collisional excitation, resonant photon transfer, and the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma [15]. The formation of an energetic reaction of atomic hydrogen was consistent with a source of free energy from the catalysis of atomic hydrogen by Sr^+ and Ar^+.

B. Balmer α line widths

The energetic hydrogen atom energies were calculated from the Doppler width of the 656.3 nm Balmer α line emitted from RF rt-plasmas [8-9]. The full half-width $\Delta\lambda_G$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \tag{10}$$

$\Delta\lambda_I$ in our experiments was $0.006\ nm$. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16\ X\ 10^{-7}\lambda_0\left(\frac{T}{\mu}\right)^{1/2} \tag{11}$$

where λ_0 is the line wavelength, T is the temperature in K ($1\ eV = 11{,}605\ K$), and μ is the molecular weight (=1 for atomic hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by ±5% corresponding to an error in the energy of ±10%.

The 656.3 nm Balmer α line widths recorded on the argon-hydrogen (90/10%)-strontium rt-plasma having a titanium filament initially and after 70 hours of operation are shown in Figure 4. Significant broadening was not observed initially. However, the Balmer α line profile of the plasma emission after 70 hours comprised two distinct Gaussian peaks, an inner, narrower peak corresponding to a slow component with an average hydrogen energy of 1 eV and an outer broader peak corresponding to a fast component of 20 eV. Only the hydrogen lines were broadened. These results are consistent with the catalysis of hydrogen to lower-states followed by subsequent transitions with increasing energy release by an autocatalytic mechanism previously reported with spectroscopic evidence [7-8].

We have assumed that Doppler broadening due to thermal motion was the dominant source to the extent that other sources may be neglected. This assumption was confirmed

when each source was considered. In general, the experimental profile is a convolution of two Doppler profiles, an instrumental profile, the natural (lifetime) profile, Stark profiles, van der Waals profiles, a resonance profile, and fine structure. The contribution from each source was determined to be below the limit of detection [1-6, 8-14, 16, 19-20, 23].

The emission spectrum from the hollow anode, glow discharge of argon-hydrogen (95/5%)-strontium (Figure 5a) showed an intense Sr^+(407.77 nm) line. The selectively Doppler-broadened 656.3 nm Balmer α line width recorded with a high resolution visible spectrometer corresponding to an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population is shown in Figures 5b and 5c. The independence of the broadening and the peak shape with position in the cell or the dependence on applied voltage or pressure over a broad range excludes the only conventional explanation of a field acceleration mechanism as discussed previously [1-6, 8-14, 16, 19-20, 23].

The formation of fast H can be explained by a resonant energy transfer from hydrogen atoms to Sr^+ or Ar^+ ions of two and one times the potential energy of atomic hydrogen, respectively, followed by a collisional energy transfer to yield fast $H(n=1)$, as well as the emission of $q \cdot 13.6\,eV$ photons reported previously [5-7]. For example, the exothermic chemical reaction of $H+H$ to form H_2 does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy- $H+H+M \rightarrow H_2+M^*$ [30]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. In the case of the catalytic reaction with the formation of states given by Eqs. (1) and (3), the temperature of H becomes very high.

C. Power balance of the rt-plasma cell

The thermogram, $T(t)$ response of the air-gap reactor with an input power of 10 W to maintain an argon-hydrogen (95/5%)-Sr^+ plasma compared to the heater calibration with stirring only and with a constant input power to the high precision heater of 10 W is shown in Figure 6a. It is evident that the value of the heating slope of the calibration experiment (heater) is smaller than the value of the reaction test, implying that for the same experimental conditions and input power, the rt- plasma transferred more heat to the water than the control performed using the high precision heater. According to Eq. (6), the water bath temperature is a direct indication of the amount of heat generated inside the reaction cell and transferred to the system; therefore, the results of this study show that the argon-hydrogen (95/5%)-strontium plasma generated heat in excess of the input power.

The average baseline corrected least squares fit of the slope, $\dot{T}(t)$, for several calibrations was $5.23\,X\,10^{-5}\ °C/s$, and the heat capacity determined from Eqs. (8-9) with $P_{ex}=0$, and $P_{in}=P_{cell}=10\ W$ was $1.911\,X\,10^{5}\ J/°C$. Then the temperature response of the calorimeter for any case (Eq. (9)) was determined to be

$$\dot{T}(t)=\left(1.911\,X\,10^{5}\ J/°C\right)^{-1}\times P_{out} \tag{12}$$

Also a plot of the evolution of excess heat as a function of time can be obtained by using the same heat capacity multiplied by the delta temperature between the reaction and calibration test profiles and further dividing by the time increment:

$$P_{ex}^{i}=\frac{C_p(T_r^i-T_c^i)}{t_i-t_0} \tag{13}$$

where P_{ex}^{i} is the excess heat, T_r^i and T_c^i are the water bath temperature of the reaction test and the calibration test at time t_i, respectively, and t_0 is the time at which the heating period started. The excess power obtained for the plasma reaction as a function of time determined by using the measured $\dot{T}(t)$, the input power of 10.0 W, and Eqs. (8) and (9), is shown in Figure 6b. The typical excess heat observed was 2.85 W. These results agree with those obtained using Eq. (13). Sources of error were the error in the calibration curve (± 0.05 W) and the measured input power (± 0.01 W). The propagated error of the calibration and power measurements was ± 0. 05 W.

Given an argon-hydrogen (95/5%) flow rate of 1.0 sccm and an average excess power of 2.85 W, energy balances of over $-7.7\,X\,10^{4}\ kJ/mole\ H_2$ ($471\ eV/H\ atom$) were measured. The reaction of hydrogen to form water, which releases $-241.8\ kJ/mole\ H_2$ ($1.48\ eV/H\ atom$) is about 320 times less than that observed. The results indicate that once an atom given by Eqs. (1) and (3) is formed by a catalyst, further catalytic transitions $n=\frac{1}{3}\rightarrow\frac{1}{4}$, $\frac{1}{4}\rightarrow\frac{1}{5}$, and so on, occur to a substantial extent. This is consistent with the series of lower-energy hydrogen lines with energies of $q\cdot 13.6\ eV$ where $q=1,2,3,4,6,7,8,9,\ or\ 11$ [5-7], the previously given theory [1-7, 27-29], and previous studies which show very large energy balances [6, 10, 14, 22-23]. These results were confirmed by Calvet and water-flow calorimetry.

4. Conclusion

An rt-plasma formed with a low field (1V/cm), at low temperatures (e.g. $\approx 10^3\ K$), from argon and atomic hydrogen generated at a titanium filament with strontium which was vaporized by heating the metal. Strong Balmer emission was observed that indicated an energy source of $>12\ eV$. The energetic reaction of atomic hydrogen was anticipated to form energetic hydrogen atoms. Significant Balmer α line broadening corresponding to an average hydrogen atom temperature of 20 eV was observed. The time-dependence of the appearance of fast H supported an energetic chemical reaction as the source. The power balance of a rt-plasma with Sr^+ and Ar^+ as catalysts was measured by water bath calorimetry. An average excess power of 2.85 W was observed. The enthalpy of formation ΔH_p of strontium hydride is $-199.1\ kJ/mole$ $(1.0\ eV/H\ atom)$ [32]. Thus, the energy for hydriding all of the 4 g (46 mmoles) of strontium would be 9.2 kJ compared to the energy released over the 25 hours of reaction time of 257 kJ. Thus, an excess power of 2.85 W measured calorimetrically on rt-plasmas with Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present was representative of the excess power. This observation supported the rt-plasmas mechanism since there is no known chemistry which could account for the observed power.

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Figure Captions

Figure 1. The experimental setup for generating an argon-hydrogen-strontium rt-plasma.

Figure 2. Air-gap reactor comprising a hollow anode DC glow discharge cell and a stainless steel jacket for maintaining an argon-hydrogen (95/5%)-Sr^+ plasma.

Figure 3. Water bath calorimetric system for measuring the power balance on an argon-hydrogen (95/5%)-Sr^+ plasma.

Figure 4. The 656.3 nm Balmer α line width recorded with a high-resolution visible spectrometer on the initial emission of a hydrogen-strontium rt-plasma and the emission at 70 hours of operation. Significant broadening was observed over time corresponding to an average hydrogen atom temperature of 20 eV.

Figure 5. (a) The emission spectrum from a hollow anode, glow discharge of argon-hydrogen (95/5%)-strontium showing an intense Sr^+ (407.77 nm) line. (b) The high resolution spectrum (653.0-659.0 nm) of the argon-hydrogen (95/5%)-strontium plasma emission showing selective broadening of the Balmer α line relative to the argon and strontium atomic lines. (c) The selectively broadened 656.3 nm Balmer α line width recorded with a high-resolution visible spectrometer corresponding to an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population.

Figures 6. (a) Water bath temperature profiles of the air-gap reactor with an input power of 10 W to maintain an argon-hydrogen (95/5%)-Sr^+ plasma compared to the heater calibration. (b) Excess power obtained for the plasma reaction as a function of time.

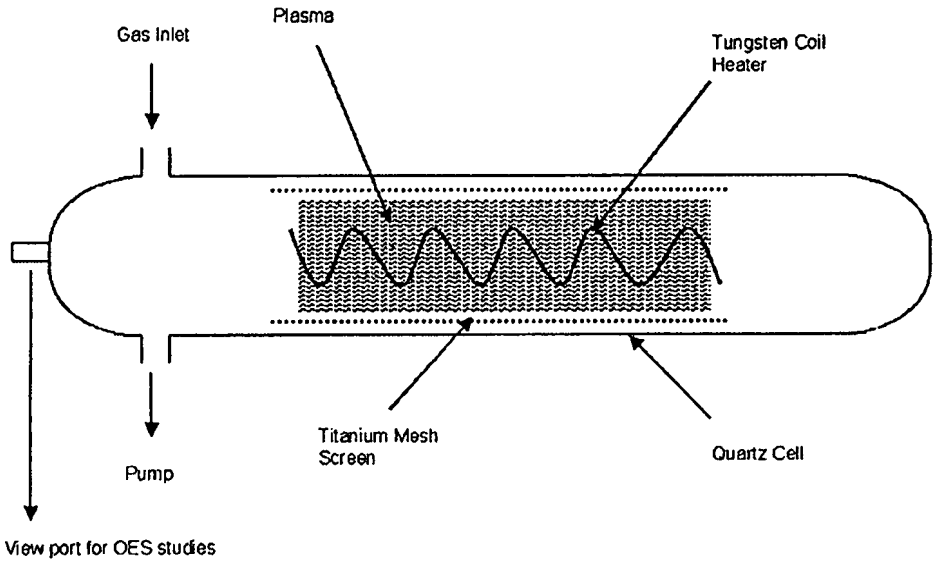
Gas Inlet
Plasma
Tungsten Coil
Heater
Titanium Mesh
Screen
Quartz Cell
Pump
View port for OES studies

Fig. 1

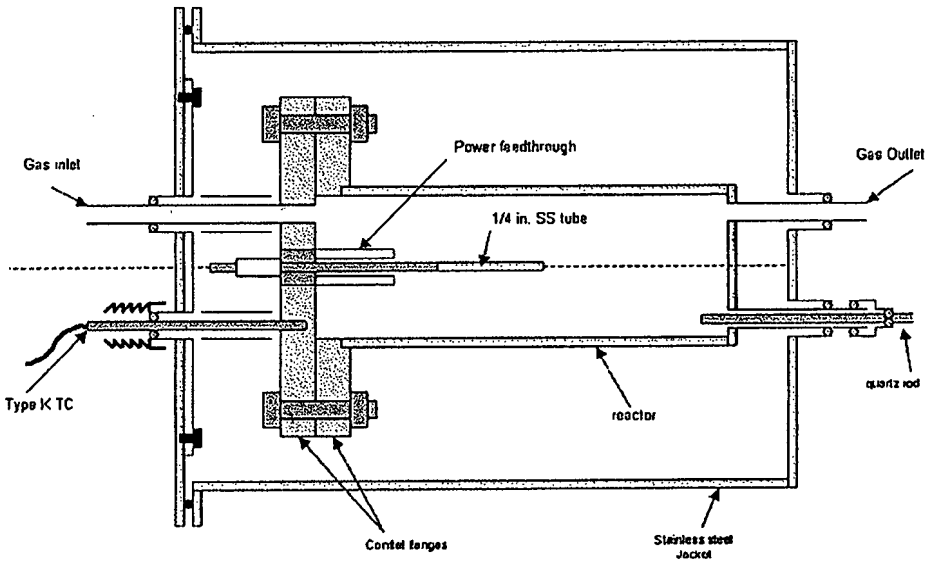
Gas inlet
Power feedthrough
Gas Outlet
1/4 in. SS tube
Type K TC
reactor
quartz rod
Conflat flanges
Stainless steel Jacket

Fig. 2

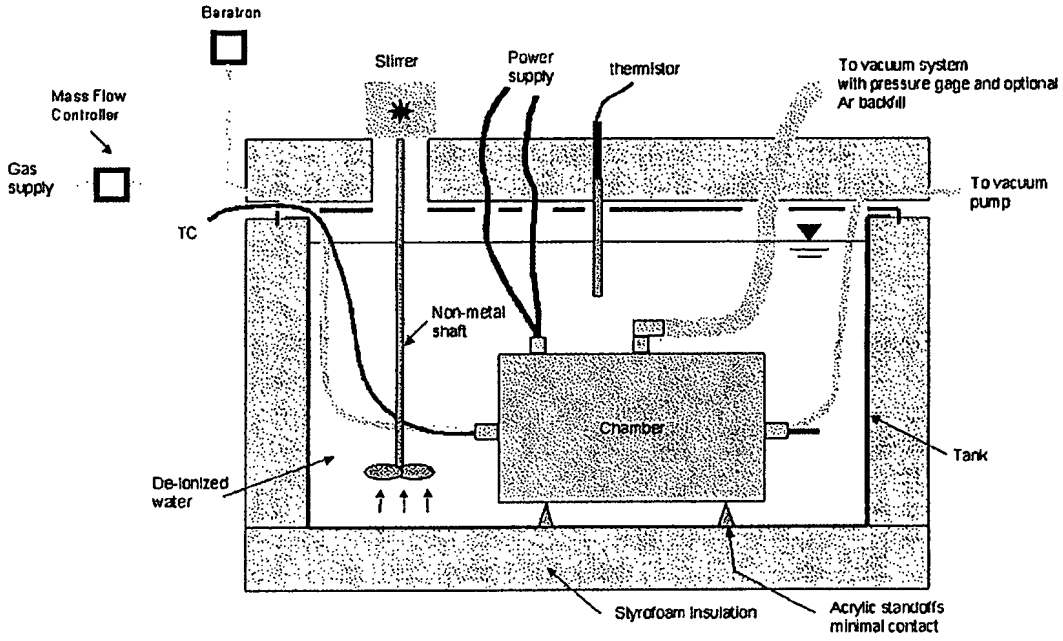
Baratron
Mass Flow Controller
Gas supply
Stirrer
Power supply
thermistor
To vacuum system with pressure gage and optional Ar backfill
To vacuum pump
TC
Non-metal shaft
Chamber
Tank
De-ionized water
Styrofoam insulation
Acrylic standoffs minimal contact

Fig. 3

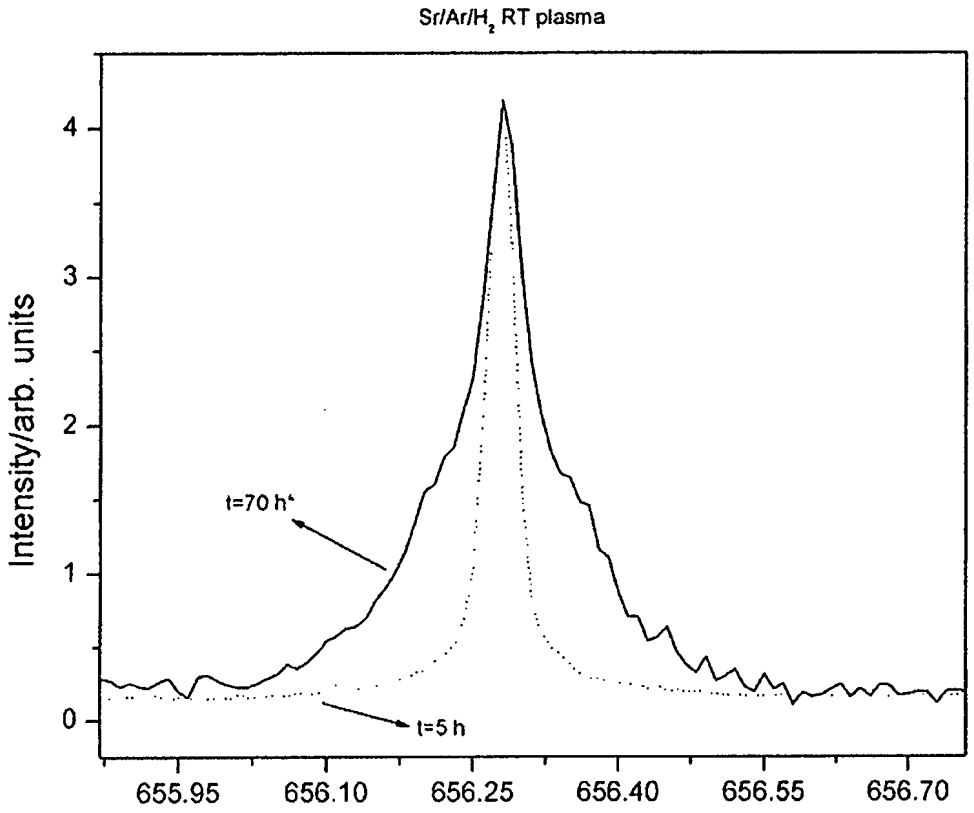
Sr/Ar/H2 RT plasma
Intensity/arb. units
0
1
2
3
4
655.95
656.10
656.25
656.40
656.55
656.70
t=70 h
t=5 h

Fig. 4

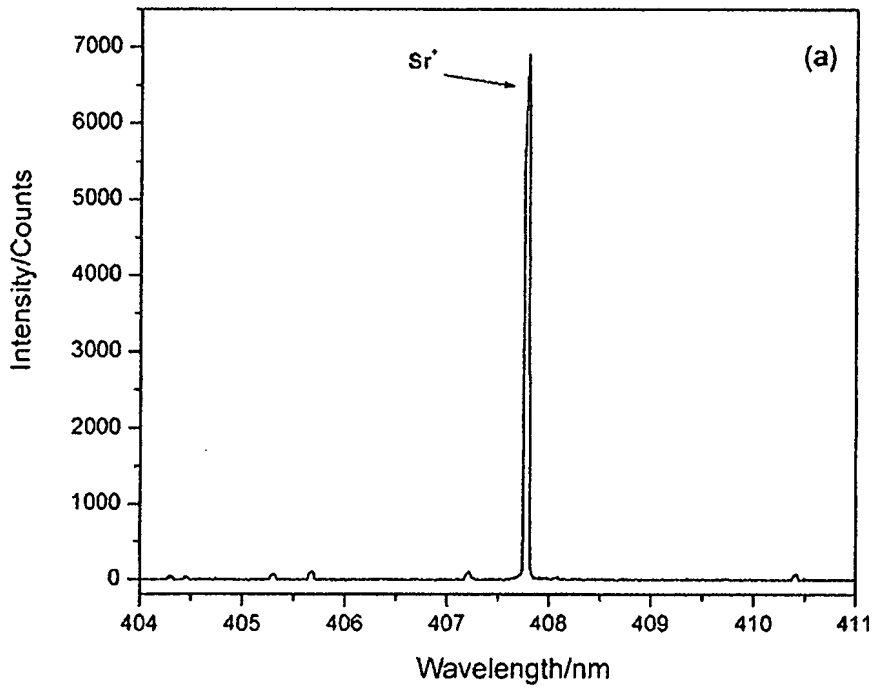
Sr'
(a)
Intensity/Counts
Wavelength/nm
7000
6000
5000
4000
3000
2000
1000
0
404
405
406
407
408
409
410
411

Fig. 5a

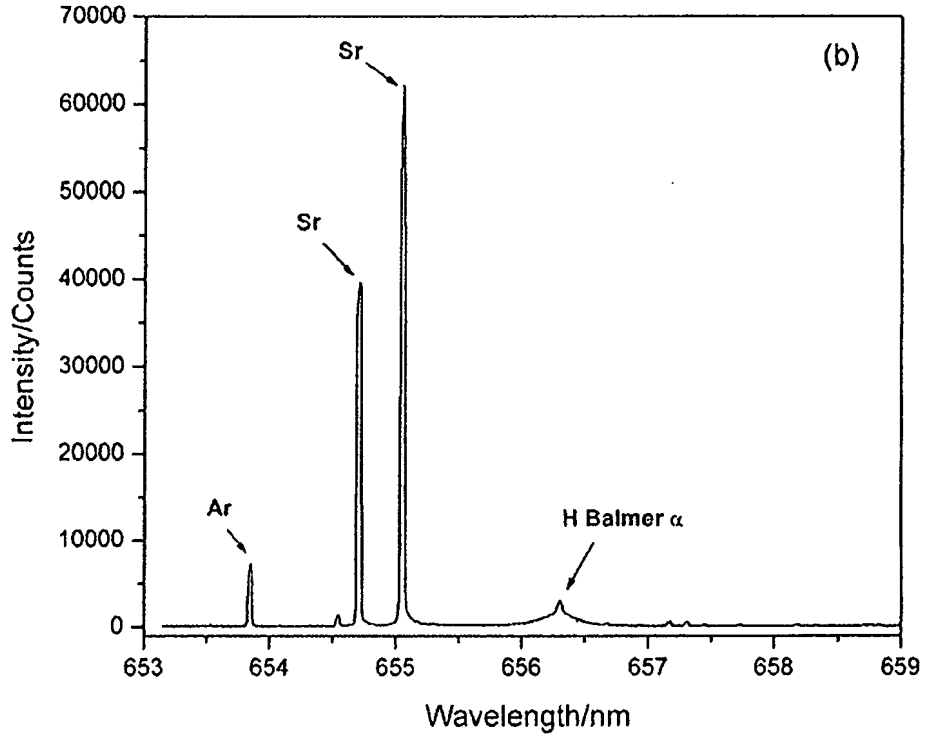
70000
60000
50000
40000
30000
20000
10000
0
Intensity/Counts
Sr
Sr
(b)
Ar
H Balmer α
653
654
655
656
657
658
659
Wavelength/nm

Fig. 5b

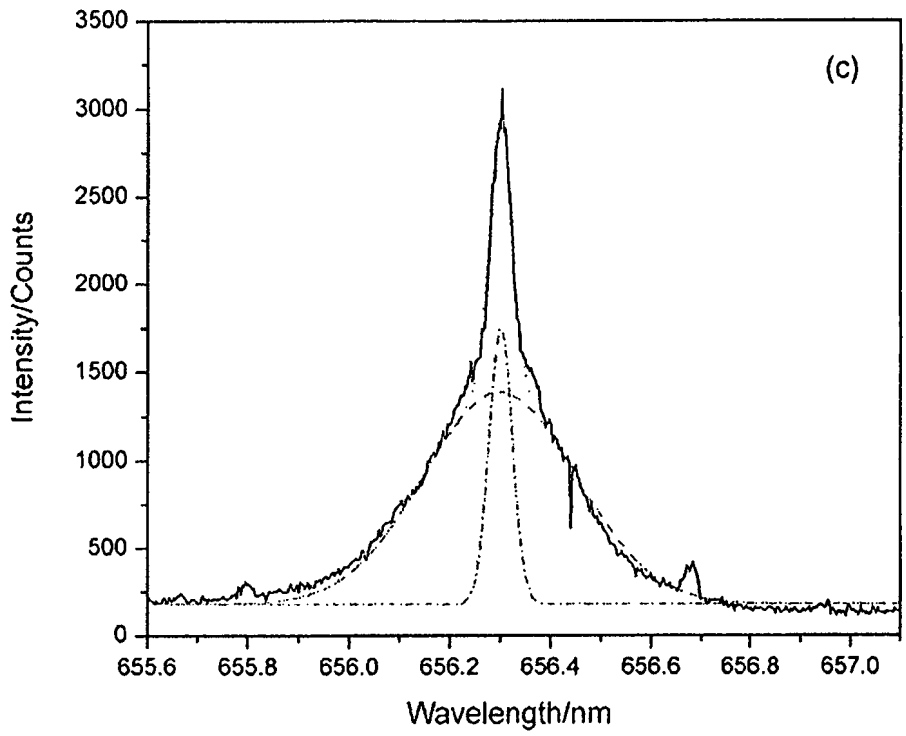
(c)
Intensity/Counts
Wavelength/nm
3500
3000
2500
2000
1500
1000
500
0
655.6
655.8
656.0
656.2
656.4
656.6
656.8
657.0

Fig. 5c

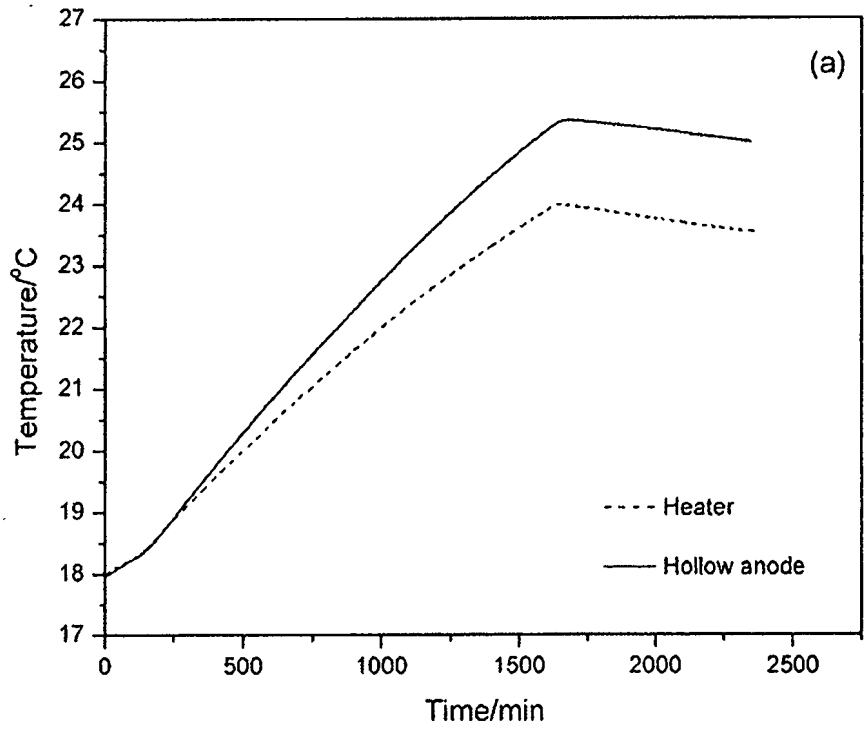
(a)
Temperature/°C
Time/min
Heater
Hollow anode
27
26
25
24
23
22
21
20
19
18
17
0
500
1000
1500
2000
2500

Fig. 6a

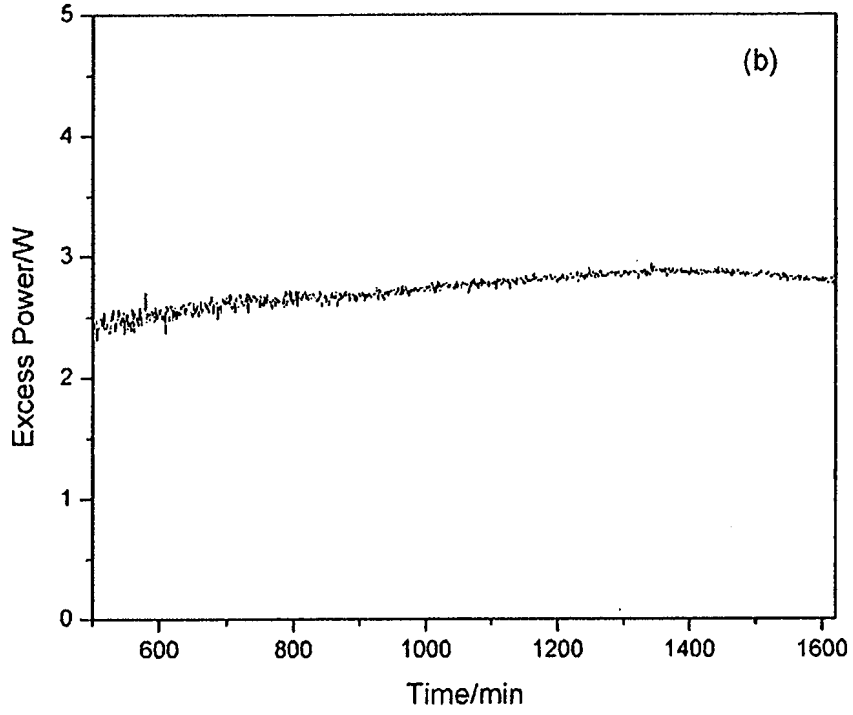

Fig. 6b